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TREATMENT OF SULPHATE IN MINE WATERS: RECYCLING PERSPECTIVE

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 22.8.2016.

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Abstract of master's thesis

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Abstract

Water treatment is essential in mining operations. Mining produces large quantities of contaminated water, which can cause irreparable harm to near water bodies. Sulphate is one of the species found in mine waters and it is particularly problematic when it is in the form of a highly soluble sodium sulphate. Sulphates in water bodies can increase salinity. Due to increasingly stricter discharge limits on compounds in effluents, it is imperative to look for ways to actively reduce the amount of sulphate in mine waters. Lately, reverse osmosis (RO) has become a very popular choice for treatment of waters with high sulphate content. RO is an effective way of purifying water because the membranes used reject salts very effectively. However, the retentate stream with high salinity causes problems because it needs treatment before it can be released into the environment.

The literature study presents the process studied in the thesis, different aspects of water in mining processes, RO process principles, and introduces different methods for the treatment of the RO retentate. These include various thermal, chemical precipitation, and membrane technologies. These methods are compared in order to determine the most promising alternative to treat the retentate and to gain a product eligible for selling or recycling back to the process. From the alternatives found, two methods, carbothermal reduction and precipitation as gypsum, are chosen to be examined further. In the applied part of the study, a model of the thermal method is simulated. It contains the concentration of the retentate, crystallisation of anhydrous sodium sulphate (Na_2SO_4), and the reduction reaction, which produces sodium sulphide (Na_2S), carbon monoxide (CO), and carbon dioxide (CO_2). This process is found to be very energy intensive and due to this and the limited amount of information found in literature, this process concept is deemed to require further studies in order for it to be ready for implementation. The precipitation as gypsum is examined through laboratory experiments. It is discovered, that the alkalinity of the retentate limits the sulphate reduction achieved. With the original retentate, a sulphate concentration of approximately 6500 mg/l can be reached. The reduction can be significantly increased by using a pH lowering agent. With the addition of hydrochloric acid (HCl), the sulphate concentration reached is circa 2500 mg/l. The use of a neutralising agent effectively prevents the concentration of sodium hydroxide (NaOH) in the solution for recycling. The precipitation process is simpler and lower in costs compared to the thermal process in addition to more abundant literature data and confirming laboratory results, and therefore, it is found to be the more potential of the two concepts studied.

Keywords Reverse osmosis, retentate, sodium sulphate, gypsum

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Tiivistelmä

Veden käsittely on välttämätön osa kaivostoimintaa. Kaivostoiminta synnyttää suuren määrän sille altistunutta vettä, jolla voi olla korjaamattomat vaikutukset lähellä oleviin vesistöissä. Sulfaatti on yksi kaivosvesistä löytyvistä ioneista ja se on erityisen ongelmallinen esiintyessään natriumsulfaattina, erittäin hyvin veteen liukenevana suolana. Vesistöissä sulfaatit lisäävät suolapitoisuutta ja aiheuttavat vesistöjen kerrostumista. Yhä tiukentuvat päästörajat kaivokselta poistettavissa vesissä esiintyville yhdisteille johtavat siihen, että on välttämätöntä löytää keinoja aktiiviseen sulfaatin määrän vähentämiseen kaivosvesissä. Viime aikoina käänteisosmoosista on tullut hyvin suosittu menetelmä suuria sulfaattipitoisuuksia sisältävien vesien käsittelyyn. Käänteisosmoosi on hyvä menetelmä tähän, koska käytetyt kalvot hylkivät suoloja tehokkaasti. Tästä huolimatta menetelmässä syntyvä suuren suolaisuuden sisältävä rejektivirta aiheuttaa ongelmia, koska myös se vaatii käsittelyä.

Kirjallisuusosassa käydään läpi työssä tutkittava prosessi, eri aspekteja vesistä kaivosprosesseissa, käänteisosmoosin periaate ja esitellään eri menetelmiä käänteisosmoosin rejektin käsittelyyn. Näihin kuuluu esimerkiksi useita termisiä sekä kalvoihin tai kemialliseen saostukseen perustuvia menetelmiä. Menetelmiä vertaillaan, jotta löydettäisiin sopivin rejektin käsittelytapa, jonka tuote voitaisiin joko kierrättää prosessissa tai myydä. Vaihtoehdoista valitaan kaksi, karboterminen reduktio ja saostaminen kipsinä, joita tutkitaan tarkemmin. Työn soveltavassa osassa kootaan malli, jolla karboterminen reduktio simuloidaan. Malli sisältää rejektin väkevöinnin ja kiteytyksen kidevedettömänä natrium sulfaattina (Na_2SO_4) sekä reduktio reaktion, joka tuottaa natrium sulfaattia, hiilimonoksidia (CO) sekä hiilidioksidia (CO_2). Prosessin todetaan olevan hyvin energiaintensiivinen, sekä siitä löytyvän rajallisen kirjallisuustiedon takia tämän prosessikonseptin todetaan tarvitsevan lisätutkimuksia, jotta se olisi toteutettavissa. Saostusta kipsinä tutkitaan laboratoriokokeiden kautta. Todetaan, että rejektin alkaalisuus rajoittaa saavutettavaa sulfaattireduktiota. Saavutettu sulfaattikonsentraatio on noin 6500 mg/l. Reduktiota voidaan parantaa huomattavasti lisäämällä pH:ta laskevaa reagenssia. Lisäämällä suolahappoa saavutetaan 2500 mg/l suuruinen sulfaattikonsentraatio. Neutraloivan reagenssin lisääminen kuitenkin rajoittaa natriumhydroksidin konsentroimista liuokseen. Saostukseen perustuva prosessi on yksinkertaisempi sekä edullisempi kuin terminen prosessi, minkä lisäksi olemassa oleva suuri määrä kirjallisuutta ja saadut laboratoriokoetulokset kipsin saostuksesta tekevät saostusprosessista potentiaalisemman vaihtoehdon.

Avainsanat Käänteisosmoosi, rejekti, natriumsulfaatti, kipsi

Preface

This study was carried out at Aalto University School of Chemical Technology in the Department of Plant Design. I wish to thank Terrafame Group Oyj for the immensely interesting and challenging thesis subject. Not often one comes across such a relevant topic for a thesis. I have learned so much and enjoyed working on this project.

Especially, I would like to thank my supervisor, professor Pekka Oinas, and my advisors, Jani Kiuru and Sarwar Golam, who have helped me with innumerable questions and problems. Yet, I was also awarded a significant amount of freedom to shape and carry out the work, which made working on the project much more meaningful. I would also like to thank Juha-Pekka Pokki for helping me design and organise my laboratory experiments, and Hannu Revitzer, for carrying out the analyses of my experiments.

Big thanks are owed to my family; my parents and my sister Katja, who have been a constant source of support in all my endeavours. Much of my interest in science and engineering comes from my grandfather Reino, who has always encouraged me to be curious. Thanks are also owed to my irreplaceable group of friends; Kirsi, Ilona, and Ella, who have never ceased to challenge and motivate me. I am also very grateful to my boyfriend Jimmy, who has lived with me through not only this project but all my years of studies, and has never ceased to support and encourage me.

Helsinki, 22.8.2016

Kaisa Kiipula

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Abbreviations

AAS	Atomic Absorption Spectroscopy
AM	Anion-exchange Membrane
AMD	Acidic Mine Drainage
BAT	Best Available Technology
BMED	Bipolar Membrane Electro Dialysis
CA	Cellulose Acetate
CM	Cation-exchange Membrane
COD	Chemical Oxidation Demand
DOE	Design of Experiment
EFC	Eutectic Freeze Crystallisation
FC	Forced Circulation
FO	Forward Osmosis
ICP	Inductively Coupled Plasma
MBR	Membrane Bioreactor
MEE-MVC	Multi-Effect Evaporation Mechanical Vapour Compression
MIW	Mine-Impacted Water
MSF	Multiple Stage Flash
PA	Polyamide
PLS	Pregnant Leach Solution
RO	Reverse Osmosis
SRB	Sulphate Reducing Bacteria
TBT	Top Brine Temperature
TDS	Total Dissolved Solids
ZLD	Zero Liquid Discharge

1 Introduction

1.1 Background

Water is an essential component in all mining operations. It is used all the way from processing and transportation of ore and waste to separation of minerals and washing of equipment. Considering how much water is needed in mining operations and the important human rights questions related to water and its usage especially in areas where clean water resources are scarce, it is evident that water management and purification have significant importance in mining. The concentrations and volumes of different contaminants in effluents from mining operations are regulated and followed closely by authorities. The tendency has lately been that the regulations and limits are becoming stricter which means that a proactive approach to environmental issues, such as effluent purification, is needed in order to secure operation's environmental basis in the future.

This study takes a detailed look at the waste water handling and chemical recycling in a specific mining operation in Sotkamo, Finland. The objective is to find a viable way of handling the retentate from reverse osmosis system, which is already in operation on site. The intention is to regenerate chemicals needed in the operation and recycle them back into the process. The focus is on the removal of two particularly problematic components, sodium (Na^+) and sulphate (SO_4^{2-}) ions, typical contaminants in mine waters and present in the retentate examined in this study. Sulphate is considered harmful when released into the environment because of its ability in many cases to acidify water, high scaling potential, and possible corrosive and purgative effect (Bowell 2004) and therefore its release into the environment is regulated. Sodium itself is not considered harmful or toxic, and therefore its discharge into the environment is so far not regulated. The problem with sodium ions in the retentate derives from the fact that with sulphate it forms sodium

sulphate ($NaSO_4$), a highly water soluble salt, which complicates the removal of sulphates from the retentate.

1.2 Objective of the study and methods used

The first objective in the literature study is to form an overall picture of the options for sulphate removal suitable for the retentate from the existing reverse osmosis system. After this, the concentration shifts to those options that are in line with the intent on gaining products suitable for recycling. Out of these technologies, the ones that seem the most viable are selected for further examination.

The applied part is a case study with the goal of constructing a recommendation for future development of purification and reuse of the retentate in a specific mining operation. This is done by utilising simulation and laboratory testing, where appropriate. Lastly, the operating costs of chosen options are evaluated.

Research questions for the study are formulated as follows:

1. Can the sulphate content in the retentate from the reverse osmosis be lowered to an acceptable level using novel technology in a feasible way?
2. Can the retentate be utilised for recycling?

1.3 Structure of the study

Chapters 2, 3, 4, and 5 make up the literature review, which presents the needed background information about the process and technologies examined in the applied part of the study. Chapter 6 consist of a review of the literature study and chapter 7 presents the case study. Chapter 8 describes the research methodology for the studies in which the most promising technology options discovered in the literature review are examined from techno-economic perspective. Chapter 9 presents the results gained from the studies, and compares the process options. Chapter 10 consists of the conclusions that are drawn from

the gained results, and lastly, focuses on the limitations of the gathered results and lists recommendations based on the project.

2 Description of the mining process

The process examined in this study is a mining process based on heap bioleaching located in Sotkamo, Finland. The ore deposit there is low-grade black schist with the following main sulphide minerals: pentlandite, pyrrhotite, chalcopyrite, sphalerite, and pyrite. (Riekkola-Vanhanen 2013) The process principle relies on a natural biological process in which bacteria present in the ore dissolve metals by oxidation. After the heap bioleaching, precipitation reactions are used to recover the metals as sulphides. (Halinen 2015) Different metals precipitate at different pH-levels, so by changing the pH level the metals can be recovered in a specific order. In the metal recovery step, a considerable amount of contaminated effluent is produced. Thus, considerable water treatment facilities are needed. (Riekkola-Vanhanen 2013) An overview of the process can be seen in Figure 1.

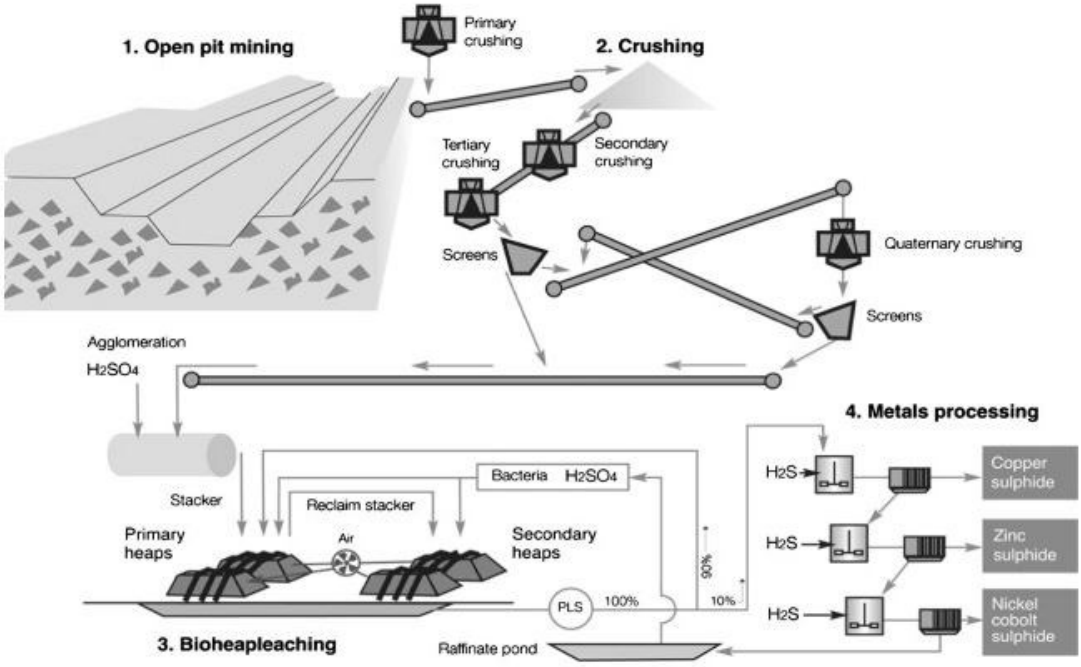

Figure 1. Process flowsheet (Riekkola-Vanhanen 2013).

2.1 Open pit mining and materials handling

In the Sotkamo mine, conventional large-scale open pit drill and blast methods are used in order to extract ore and waste. Ore is crushed and screened in four stages. The primary crushing is followed by three phases of crushing and screening in the fine crushing station. After this, all material above the size 10 mm is led to agglomeration, where in a rotating drum pregnant leach solution (PLS), referring to acidic metal-laden solution, is mixed with the ore. This consolidates smaller particles with coarser particles, which in turn makes the ore permeable to air and water. This is the requirement for the success of the following heap bioleaching. (Riekkola-Vanhanen 2013)

2.2 Heap bioleaching

Bioleaching is a process that utilizes microorganisms in extracting metals from ores containing sulphide and/or iron. In the process, iron and sulphide go through microbial oxidation and produce ferric ion (Fe^{3+}) and sulfuric acid (H_2SO_4). With these chemicals, it is possible to convert insoluble metal sulphides into metal sulphates, which in turn are soluble. These metals include, for example, copper, nickel, and zinc. The formed sulphates are recoverable relatively easily from the solution. (Rawlings et al. 2003) Leaching of the metals from sulphide minerals is based on the attack of the ferric ion (Fe^{3+}) and hydrogen ion (H^+) directed at the metal sulphide bond. The attacking ions are formed in the microbial oxidation. Reactions that are included in this mechanism can be seen below. Reaction 1 is a chemically catalysed reaction, reactions 2 and 3 are bacterially catalysed reactions, and reaction 4 is both chemically and bacterially catalysed reaction. One of the advantages with this technology is that it is suitable when dealing with ore deposits with valuable metal content below 0.5 % (w/w). Above these metal concentrations, pyrometallurgical processes become more feasible. (Halinen 2015) The former is the case with the mining operation examined in this study.

$$MS + 2Fe^{3+} \rightarrow M^{2+} + S^0 + 2Fe^{2+} \quad (1)$$

$$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (2)$$

$$4Fe^{2+} + O_2 + 2H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (3)$$

$$MS + 2O_2 \rightarrow M^{2+} + SO_4^{2-} \quad (4)$$

Where M equals metal.

In the Sotkamo mine, a version of this technology called heap bioleaching is used. In heap bioleaching, the grinded and agglomerated ore is gathered into heaps that are irrigated from the top with acidic water called leach liquor. The leach liquor subsequently percolates through the heap, is collected from the bottom as pregnant leach solution (PLS), and is circulated back to the top pf the heap. The PLS can either be collected and replaced once the metal concentration has reached high enough levels or alternatively a small side stream can be taken continuously for metal recovery. (Halinen 2015)

The metal sulphates are enriched using PLS that is circulated into the primary heaps for a time period of 13 – 14 months, after which the leached ore is collected, moved, and reassembled in the secondary heap pad, where the leaching is continued for the parts in the ore that were in poor contact with leaching solution. (Riekkola-Vanhanen 2013)

2.3 Metal recovery

Metals in the mining operation in Sotkamo are recovered from the PLS as sulphides using pH adjustment and hydrogen sulphide. The pH dependence of metal sulphide solubilities is presented in Figure 2.

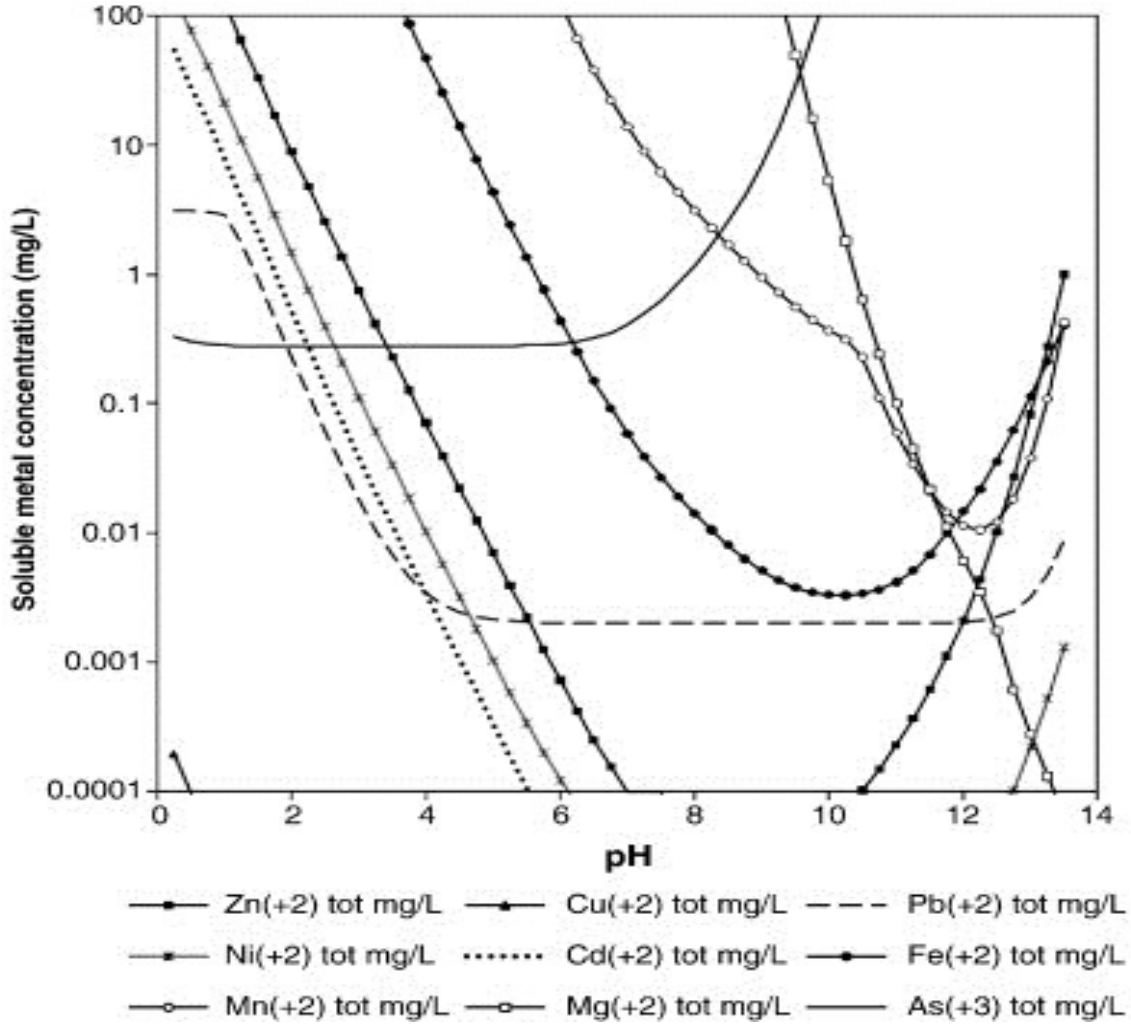

Figure 2. The pH dependency of metal sulphide solubility (Lewis 2010).

The PLS is led to copper (Cu) and subsequently to zinc (Zn) sulphide precipitation steps, where hydrogen sulphide is added to precipitate the metals. Copper and zinc precipitation cause the formation of acid, which in addition to the acidity in the feed leads to need for neutralization. Therefore, after the zinc sulphide precipitation, the PLS is led to the pre-neutralisation, which is carried out using limestone ($CaCO_3$). After the pre-neutralization stage, nickel (Ni) and cobalt (Co) are precipitated by adding hydrogen sulphide to the PLS in one stage as a mixed nickel cobalt sulphide product. The neutralisation agent in this stage is sodium hydroxide (NaOH). Iron is then extracted from the solution as goethite and hydroxide by adding limestone and oxygen. During this stage, as the pH rises, a

substantial amount of aluminium (Al) is also precipitated from the solution as hydroxide. Manganese and magnesium, which are still present in the solution, are removed in final precipitation, which is done with CaO. The products from the metal recovery are therefore copper and zinc sulphides and a mixed nickel cobalt sulphide. (Riekkola-Vanhanen 2013)

2.4 Water treatment

Water from the final precipitation stage contains a considerable amount of sodium sulphate (Na_2SO_4). The reason for this is that the reduction of the high amount of sodium in the wastewater stream is not possible using precipitation with lime. Also, the solubility of $CaSO_4$ limits the precipitation of calcium sulphate ($CaSO_4$) and a certain amount of the compound remains dissolved in the treated stream. Therefore, the stream from the final precipitation contains considerable amounts of both Na^+ and sulphate SO_4^{2-} ions, and also some Ca^{2+} -ions. This leads to the need for treatment of the overflow stream from final precipitation.

The usual options for the reduction of sulphate in mine effluents are membrane technologies, mineral precipitation methods or biological mechanisms (INAP: International Network for Acid Prevention 2003). In the case of the Sotkamo mine, a membrane process, namely reverse osmosis (RO), is in use. Some of the overflow stream from final precipitation is led to an RO system. Membrane technologies are often considered somewhat unsuitable for mine effluents, because of scaling issues, but when appropriate pre-treatment methods are applied, membrane technologies can be very effective approaches.

2.5 Environmental aspects

There has been much debate about the possibility of long-term environmental impact from the use of bioleaching technology. In general, the production process is considered environmentally friendly. However, effluents from bioleaching are released to the

environment it can lead to serious problems. These effluents are acidic and they contain metals, sulphate and iron. This is why the effluents from operations utilising bioleaching need to be neutralised or precipitated chemically. (Halinen 2015) Problems arise also, when large amounts of water are gathered inside the mine site. Problems arise when rainwater or snowmelt comes into contact with contaminated effluent water. Therefore, successful water management is paramount in mining.

3 Water in mining processes

Water is an integral part of mining and therefore special attention should be paid into sustainability management. The goal of this chapter is to give a general understanding about the role of water and water management in mining operations. The chapter discusses briefly how water is used in mining, presents typical mine water contaminants, and goes over the reasoning behind recycling and purification of mine waters.

3.1 Water usage in mining

Water is needed in numerous parts of mineral and metal processing operations (Ramachandra Rao 2006). For example, water is used to process and transport ore and waste, to separate minerals, suppress dust, wash equipment, and for human consumption (Kemp et al. 2010). It is also used in heat exchange systems and it is a reagent in hydrometallurgical operations (Ramachandra Rao 2006). When water is extracted from surface and groundwater, it can have a direct impact on ecosystems and this can lead to competition for access with other users. In order to ensure the security of the water supply, it is most often necessary to have water storage systems, such as dams or mining voids, in place. On the other hand, in wet climates or in the case of water abundance, events of extreme rainfall may lead to the surplus water in these storage facilities to be discharged into local waterways. This can have potentially serious social and environmental effects. (Kemp et al. 2010) Table 1 presents different aspects of water use in base metals refining and compares different processes. It is clear, that hydrometallurgical processes are the most water intensive of the ones compared. In those processes water has most applications and they entail numerous possible environmental consequences.

Table 1. Comparison of different aspects of water use in base metals refining (Norgate, Lovel 2004).

Aspect	Mineral processing	Pyrometallurgical	Hydrometallurgical
Water use	Transport	Utilities (cooling) Pollution abatement Granulation	Reaction medium Transport Utilities Pollution abatement
Inventory	Very large	Small	Large
Re-use	Very high	High	Moderate to high
Water quality	Raw to potable	Raw to potable	Potable to demineralised
Losses	Entrainment, Evaporation	Evaporation	Inventory Evaporation Spills/releases Products
Environmental impact	Consumption Suspended solids	Consumption Thermal Acidification (via atmospheric transport)	Consumption Ecotoxicity Eutrophication Acidification Chemical oxygen demand Suspended solids

An important part of mining is also the disposal of waste and wastewater after the recovery of valuable products. Typical systems for managing mine waste include waste rock dumps and conventional tailings. In the event of failure of these systems, substantial harm can incur to local water resources. Another serious threat to water resources is acid and metalliferous drainage (AMD), which refers to the outflow of acidic water from mines, and which is caused by the decomposition of minerals related to ore bodies in the surficial environment. (Kemp et al. 2010) The source of AMD is sulphide-containing material when exposed to oxygen and water. This mechanism is typical in iron sulphide – aggregated rocks. (Akcil, Koldas 2006) AMD is considered one of the worst and most durable after effects of mining operations globally (Kemp et al. 2010).

3.2 Mine water contaminants

There is usually a need to treat mine water before it can be re-used or released into the environment. The aim of treatment is most often to decrease acidity or to extract metals,

salts in their dissolved state or suspended solids. Included is also the material from biological sources and microorganisms. Table 2 lists the most common contaminants found in mine waters and their usual sources. (Norgate, Lovel 2004)

Table 2. Contaminants on mining sites and their sources (Norgate, Lovel 2004).

Contaminant	Typical source
Metals – Iron, manganese, zinc, lead, copper	Pyrite oxidation in underground stopes & surface rock and sand dumps & slimes dams with dissolution of metals
Sulphate	Pyrite oxidation in underground stopes & surface rock and sand dumps & slimes dams to produce sulphates
Cyanide	Spillage from plant areas, ruptured slimes delivery pipelines and slimes dams
Suspended solids	Inadequate underground settling, runoff from surface rock, sand dumps & slimes dams
Sodium	Fissure water, addition of sodium-based neutralization chemicals
Chlorides	Fissure water
Nitrogen compounds	Waste explosives, gas by-products from explosives, sewage and contaminated runoff from hostels
Phosphates	Sewage and contaminated runoff from hostels
Acidity	Pyrite oxidation underground, surface dumps (rock, sand & slimes), spillage from plant areas
Radionuclides	Pyrite oxidation in underground stopes & surface rock and sand dumps & slimes dams with dissolution of radionuclides
Microbes – faecal coliforms, coliphages	Faecal contamination of underground mine service water, poorly treated sewage, runoff from hostel areas, livestock grazing

3.3 Sodium sulphate as a mine water contaminant

Sodium sulphate is an ionic compound that is found in nature as Glauber's salt, mineralogically called mirabilite, and as thenardite, the anhydrous sulphate. In addition, sodium sulphate is a constituent of numerous compound minerals, for example glauberite, vanthoffite, bloedite, and aphthitalite, and it is a component in the waters of many natural brines and playa lakes. (Wells 1923). In addition to the natural occurrences and direct manufacturing of sodium sulphate, it is also formed as a by-product in a number of different chemical processes. Sodium sulphate ends up in industrial and mining effluents also due to different chemicals used in these processes. In the case of Sotkamo mine, sodium hydroxide is used in metals precipitation, which leads to sodium ending up in the process stream. Sulphate is found in the mine waters due to the nature of the ore in the Sotkamo mine, namely sulphide ore.

Sodium sulphate has a peculiar characteristic behaviour in some physical phase transformations, like dissolution and crystallisation. The compound dissolves into water most in a set temperature of 32.38 °C. The dissolution of sodium sulphate is endothermic, which leads to the cooling of the solution, even more so with the dissolution of crystalline hydrate. When the goal is to crystallise sodium sulphate without water, higher than the aforementioned temperature is needed. In this case, a white monoclinic crystalline salt, which is water-soluble, is formed. The melting point is 884 °C and the density in 20 °C is 2.67 g/cm^3. At temperatures below 32.38 °C, sodium sulphate is crystallised from the solution as Glauber's salt $Na_2SO_4 \cdot 10H_2O$. As a result, large, transparent, and monoclinic crystals, which decompose easily with the effect of air, are gained. The solubility of the salt in water in 30 °C is 92.7 g/100 cm^3. The melting point is 32.38 °C, at which temperature the salt dissolves into its crystal water. The density is 1.464 g/cm^3. By heating, the hydrate loses its crystal water in 100 °C. (Karamäki 1983, pp. 306 – 307) Table 3 lists the main properties of both Thenardite (Na_2SO_4) and Glauber's salt ($Na_2SO_4 \cdot H_2O$).

Table 3. Properties of sodium sulphate (von Plessen 2000)

Property	**Thenardite Na_2SO_4**	**Glauber's salt $Na_2SO_4 \cdot H_2O$**
M_r	142.04	322.19
Crystal water, %	0	55.914
mp, °C	884.0 (decomp.>884 °C)	"melts" at 32.384 °C in its own crystal water (decomp. >32.384 °C)
Crystal habit	rhombic	monoclinic
Unit cell dimensions	0.586, 1.23, 0.982	1.143, 1.034, 1.290 (angle = 107 ° 40')
No. Of molecules in unit cell	8	4
Refractive indices n_D	1.464, 1.474, 1.485	1.394, 1.396, 1.398
Density, g/cm^3	2.697	1.468
Specific heat capacity c_p at 300 K, J kg^{-1} K^{-1}	899.2	1825.7
Heat of fusion, kJ/kg	147.98	214.52
Heat of solution at 18 °C, kJ/mol	16.2	-243.8
Enthalpy of formation, kJ/mol	-1385	-4327
Entropy S °, Jmol^{-1} K^{-1}	149.6	588.2
Dielectric constant (at 10^3 Hz)	7.8	7.9
Mohs hardness	2.7	1.5 – 2

The solubility of sodium sulphate in water can be seen in Figure 3. The previously mentioned transformation point of 32.384 °C, below which Glauber's salt and above which anhydrous thenardite is crystallised, can be seen clearly in the figure. The accuracy of the temperature in which this transformation occurs makes it an appropriate fixed point. The solubility of sodium sulphate can be reduced by the presence of sodium chloride in the system. In addition to this, the presence of sodium chloride also lowers the transformation temperature to 17.9 °C. The effect of NaCl has its uses in industrial production of sodium sulphate. About the chemical properties of sodium sulphate, it is important to note that in moist air, the anhydrous form absorbs water of crystallisation, which leads to significant volume increase during the conversion to Glauber's salt. Glauber's salt is not hygroscopic, after a few days in cold air current, it is effloresced and converted to nearly anhydrous sodium sulphate. (von Plessen 2000)

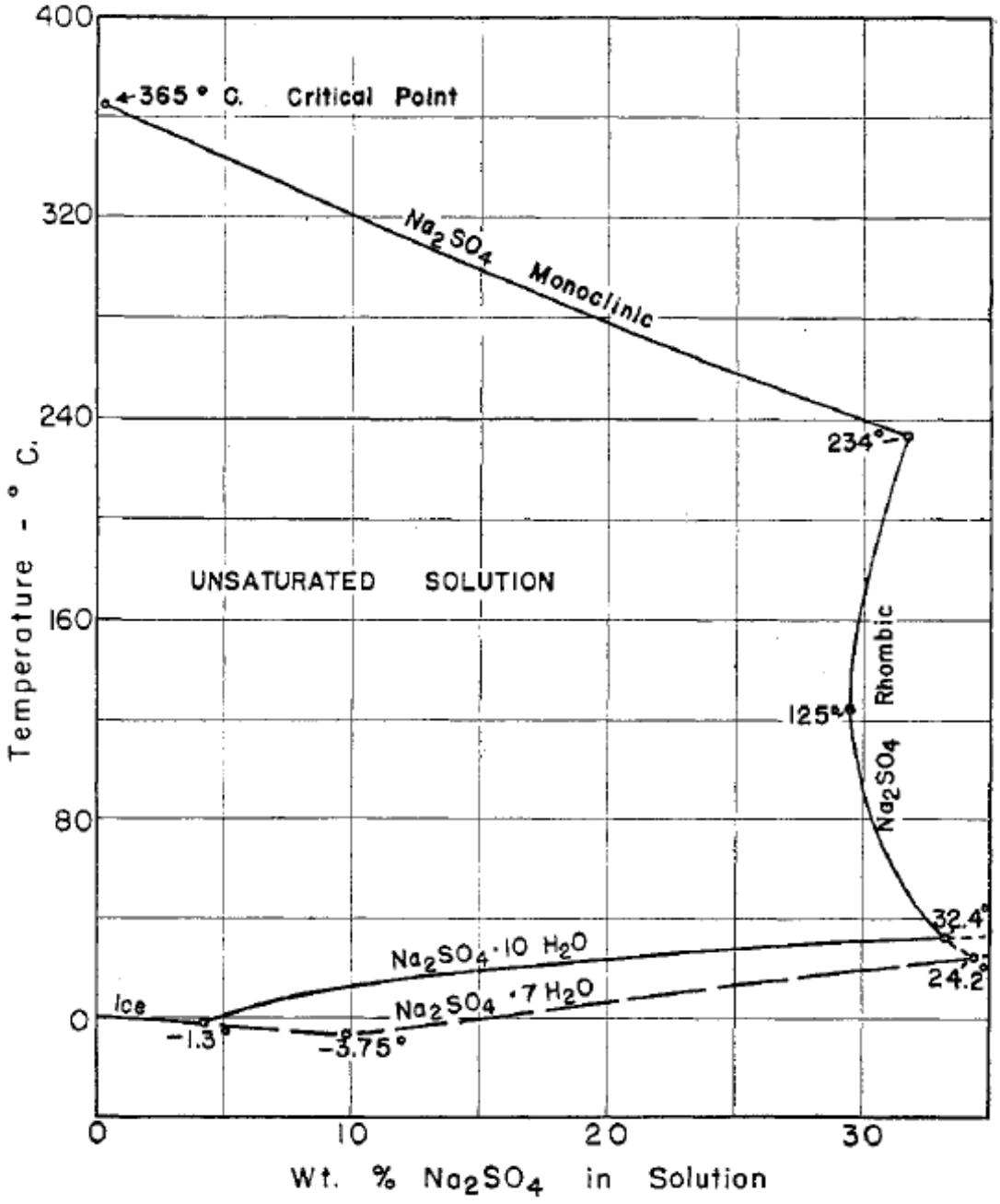

Figure 3. The solubility of sodium sulphate in water (Vener, Thompson 1950).

Sodium salts also have an effect in the boiling points of solutions containing them. This has to be taken into consideration when treating waters containing them with thermal methods. The boiling point rise caused by sodium sulfate can be seen in Figure 4.

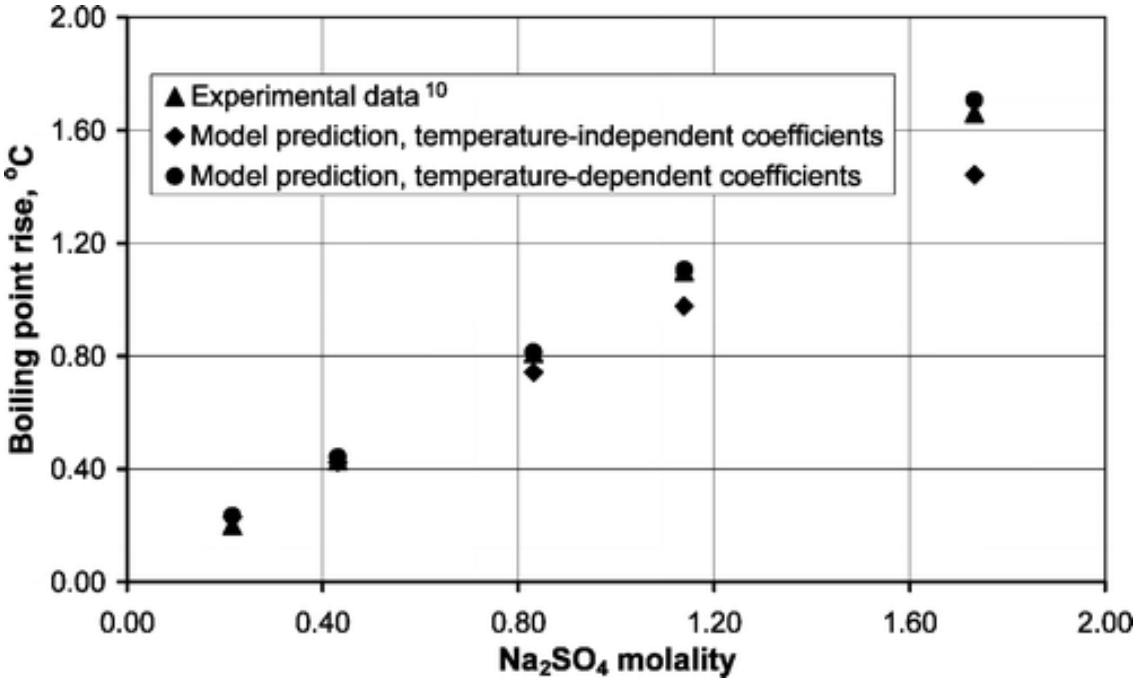

Figure 4. The boiling point rise in sodium sulphate solutions (Bialik et al. 2008).

The limitations on sulphate concentrations in effluents allowed to be released into the environment differs greatly around the world. Table 4 lists some of the sulphate limits by different authorities.

Table 4. Recommended maximum sulphate levels in different countries (Bowell 2004)

Country	Sulphate (mg/l)
USA (effluent)	500
Canada (effluent)	1,000
EU guide limit	1,000
South Africa (effluent)	600
Australia	1,000
WHO (guideline for drinking water)	250

3.4 Water management in mining operations

There are two primary objectives for the recycling of water in mining. These are the reduction of the demand for fresh or raw water and the decreasing of the volume of effluent, possibly in need of treatment, out of the process. (Norgate, Lovel 2004) In addition, recycled effluent offers a constant and reliable source of water. Effluent volumes are also usually considerable and their release into the environment either treated or non-treated can have serious effects in natural water bodies, which are prevented when recycling the effluent or part of it. In some cases, effluent water also contains considerable concentrations of organic and inorganic nutrients, e.g., nitrogen and phosphate. These nutrients can be used as fertilisers when effluent is recycled and used for irrigation. (Toze 2006) Other reasons for water recycling can also be determined, here are mentioned the ones most obvious relating to mining.

The recycling of mine water usually requires some type of treatment. Table 5 lists the water treatment methods favoured in mining industry. Lately, much attention has been given to the development of membrane technologies. The treatment and re-use of mine waters has become a good method to reduce the total water consumption and also to decrease contaminated water volumes that might require purification (Norgate, Lovel 2004). Recycling is especially important when the mining process in question is a water intensive one, such as bioleaching.

Table 5. Typical methods for mine water treatment (Ramachandra Rao 2006, from Rao and Finch 1988)

Category	Method	Application
Chemical reaction	Precipitation	Removal of alkaline earth and heavy metal ions
	Oxidation, e.g., by ozone	Oxidation of most high molecular weight organics to simpler molecules
Adsorption on solid or at an interface	Adsorption on active carbon or coal	Removal of most organics
	Adsorption on mineral slimes	Removal of metal ions and some organics depending upon the slime composition
	Adsorption on bentonite clay	Removal of metal ions and slimes
	Adsorption at liquid-gas interface	Removal of highly surface-active organics (e.g., alkyl sulphates)
Other methods	Biological oxidation	Removal of biodegradable organics
	Ion exchange resins	Removal of ionic species
	Reverse osmosis	Removal of electrolytes
	Atmospheric freezing	Removal of electrolytes and organics

Cogho and van Niekerk (2009) depict a case study from South Africa, in which a long term water management strategy of a multi-product mine is presented. The approach at the site is the following. Firstly, responsible mining and land use practises are used to minimise the amount of contaminated water produced. Secondly, with the aim of the mine being self-sufficient on water, impacted water is recycled in the mining process. The excess of the mine-impacted water (MIW) is treated in order to be eligible for discharge or to be used by the communities surrounding the site. This approach also requires that excess reclaimed water be construed as a resource, which means that mine is seen as both local and regional water supplier. It is also important to note that the water resource remains in place even after the conclusion of the active mining operation. This calls for diverse reclaimed water users, meaning also those in place even post mining. (Cogho, van Niekerk 2009)

When considering water management, there are uncertainties that are inevitable and risks that require constant managing. Examples of different types of uncertainties can be seen in Table 6. These lead to water management strategy that is dynamic and ongoing by nature, and contains assessing and quantifying risk in addition to the ability to adapt the tactics according to changing circumstances. In order to achieve these goals, a mine in South Africa has formed an integrated water management plan with annually performed updates. (Cogho, van Niekerk 2009)

Table 6. Uncertainty types and examples related to water management (Cogho, van Niekerk 2009).

Type of uncertainty	Examples
Uncontrollable variables	Future rainfall events, possible global warming effects
Technical uncertainties	Actual vs. predicted recharge through rehabilitated spoils
Economic uncertainties	Long term value of potable water
Mining related uncertainties	Mine plan, strategies around water management, possible usage of storage available in areas that are mined out

4 Reverse osmosis

Reverse osmosis is used in the treatment of mine waters quite widely. It is an established method for the removal of electrolytes and for gaining extremely pure water for recycling. This method has been applied also in the Sotkamo mine, which is why this technology is presented here in more detail.

4.1 Principle

Reverse osmosis is a pressure-driven membrane process, in which a semi-permeable membrane is used to reject the dissolved components in the feed water (Malaeb, Ayoub 2011). The causes for the rejection phenomena are size and charge exclusion and physical-chemical interactions existing between solute, solvent, and membrane (Bellona, Drewes 2005, Radjenović et al. 2008). The semi-permeable membrane separates strong and dilute solutions from each other. The amount of hydraulic force in the system depends on the concentration differential across the membrane. This determines how strong a tendency water has to permeate to the concentrated solution. Hydraulic force equals to the system's osmotic pressure. In the case of reverse osmosis, the water is forced through the membrane against osmotic pressure. This is achieved by applying an external hydraulic pressure to the saline solution. (Bowell 2004) The basic principle is that a solution containing a component with a low molecular weight is separated from the solvent by a membrane in conjunction with a hydrostatic pressure difference that is applied across the membrane, which causes a flux of solvent from the solution into the pure solvent. (Strathmann 2011) Reverse osmosis yields a very clean product, called permeate, and a very concentrated retentate. The principle of reverse osmosis can be seen in Figure 5.

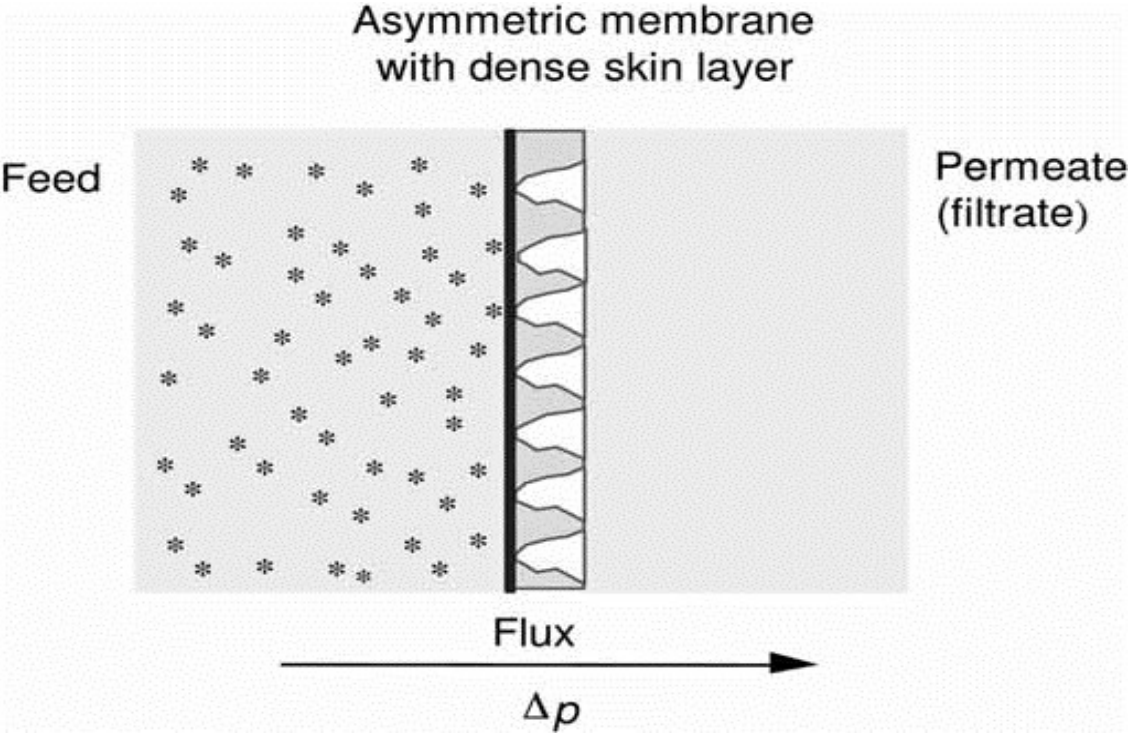

Figure 5. The principle of reverse osmosis (Strathmann 2011).

The efficiency of the reverse osmosis process is dependent on operational parameters in addition to the properties of membrane and feed water (Malaeb, Ayoub 2011). The most important limiting factor in RO processes is fouling, which is caused by clogging of the pores or the solutes being adsorbed on the membrane surface. In addition to fouling, an important question to be answered, when considering reverse osmosis processes, is how to handle the retentate streams formed in the processes so that they pose as small a threat to the environment as possible. (Van Der Bruggen et al. 2003)

The product stream in pressure-driven membrane processes is called the permeate. In RO, permeate consists of ultrapure water. This is because RO processes reject monovalent and multivalent ions, small organic compounds, macromolecules, and particles. (Van Der Bruggen et al. 2003) While the product of reverse osmosis is extremely clean, the method still produces a considerably concentrated retentate that needs to be handled. RO provides a favourable solution for the production of clean water but leaves the problem of harmful

compounds intact. A typical way of handling the retentate in power stations with the aim of zero discharge systems is to evaporate the retentate in order to produce minor volumes of extremely concentrated brines (Pervov et al. 2015).

4.2 Reverse osmosis membranes

The membranes used in RO consist of several layers of different nature. The function of the thin active layer is to separate the solutes and water. In RO applications the thickness of the active layer is approximately 0.1 – 2 μm. The thinness of the layer is a requirement for having an effective flux of water. In addition, there are thicker layers, which are more porous and are there to provide structural integrity. Without these additional layers, the active layer would be unable to withstand the feed pressure required in RO. (Howe et al. 2012, pp. 331 – 332)

There are two methods for the manufacture of membranes with multiple layers. The manufacture of asymmetric membranes is carried out using a single material, which is developed into active as well as the supporting layers in the course of the casting process. The other type of RO membrane are thin-film composite membranes that differ from asymmetric membranes so that they consist of two or more materials, which are cast on top of each other. The benefit of the latter type is that separation and structural properties can be optimised separate from each other. This is accomplished using suitable materials for each of the functions. In addition, this method enables the placement of the active layer very thinly. (Howe et al. 2012, pp. 331 – 332)

The physical and chemical properties of the material used have a strong effect on the membrane performance. The ideal would be to have a material that can provide a high flux free from fouling and clogging, in addition to being physically durable, stable chemically, not biodegradable, chemically resistant, and economical. Cellulose acetate (CA) and polyamide (PA) derivatives are the most often used materials for RO membranes. The former is typically used for asymmetric membranes while the latter are

favoured for thin-film membranes. PA membranes are chemically and physically more stable than CA membranes and when in similar temperature and pressure conditions they usually generate greater water flux and salt rejection. But, PA membranes are also more hydroscopic and have greater potential to fouling than CA membranes. PA membranes also do not tolerate free chlorine in any concentrate levels. (Howe et al. 2012, pp. 331 – 332)

4.3 Use of reverse osmosis in water purification

In reverse osmosis, dense membranes without predefined pores are used. The resulting permeation is slower than with other pressure-driven membrane processes and the rejection mechanism is solution-diffusion instead of sieving. The low permeability reached with RO (0.05 – 1.5 LMH/bar) requires considerable pressures, which leads to high energy consumption. Of course this effect is yet stronger if there is osmotic pressure caused by large concentrations of dissolved components. This is because osmotic pressure counteracts the effect of the exerted pressure. (Van Der Bruggen et al. 2003)

Reverse osmosis is currently used widely in applications of water treatment and desalination. These applications include semiconductors, food processing, power generation, pharmaceuticals, desalination biotechnology, textile, pulp and paper, mine and diary wastewater, and process and boiler water, to name a few. In mine water purification, pre-filtration has been found necessary in order to avoid fouling of the membrane. (Malaeb, Ayoub 2011) This, of course, raises the investment and operating expenses of using reverse osmosis system in mining applications.

Pre-treatment is necessary in practically every RO system. Pre-treatment is used to prevent scaling in the presence of slightly soluble salts. The removal of water from the feed concentrates the solutes, which can lead to higher concentrations than the solubility product of different salts. If no pre-treatment method is used, precipitates of these salts can appear on membrane surface, which blocks the membrane. Scaling is controlled using

either pH adjustment, antiscalants or both. Solubilities of the salts can be altered by adjusting pH while precipitate formation and its rate can may be influenced with antiscalants. As was mentioned already, filtration for particle removal is another pre-treatment method. If no backwash cycle is used, the result can be clogged feed channels or particle accumulation on membrane surface. Minimum requirement is cartridge filtration with a 5-µm strainer opening. As additional pre-treatment granular or membrane filtration is used if necessary. In order to prevent biofouling, disinfection is used as a pre-treatment method, but its use requires membrane material compatible with disinfectants. Pre-treatment is followed by pressurisation of feed water with feed pumps. (Howe et al. 2012) Figure 6 depicts a typical RO system arrangement.

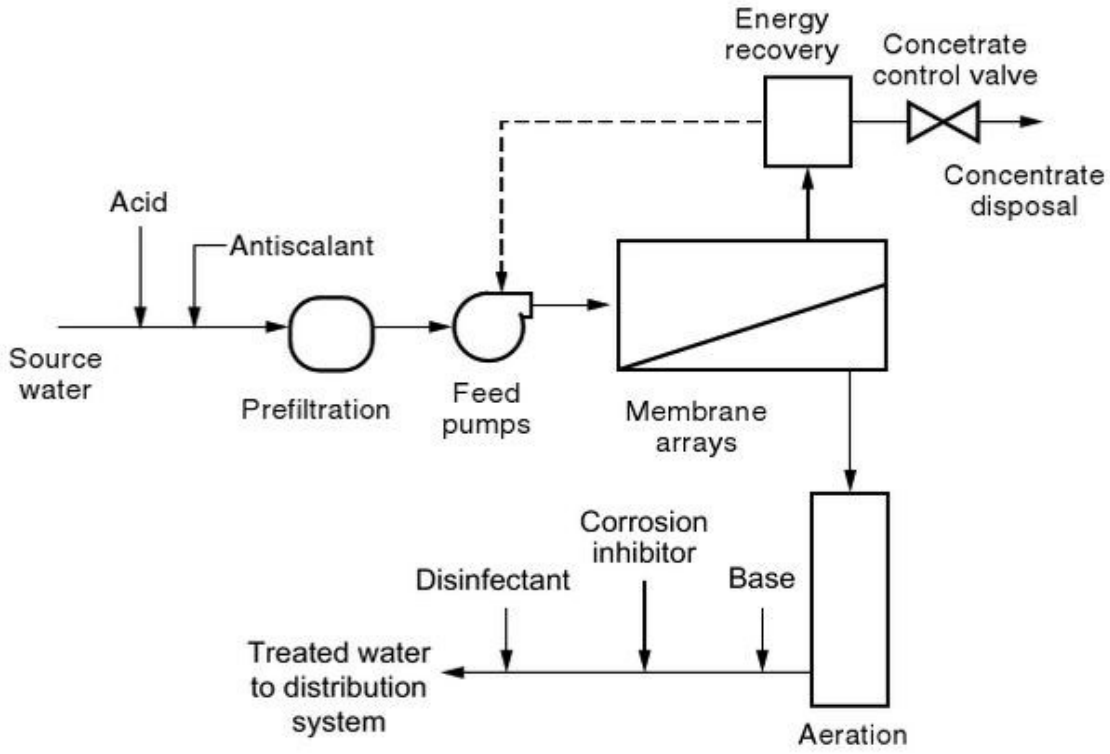

Figure 6. Typical arrangement of an RO system (Howe et al. 2012, pp. 333)

5 RO retentate treatment

In this chapter, different retentate treatment options suitable for the process examined in the study, and compatible with the objectives set for the study are presented and compared. A comparison table of these options is presented as APPENDIX I.

5.1 Understanding the problem

The retentate products of RO systems are highly concentrated solutions in comparison with the RO feed stream. One of the most important questions related to the use of reverse osmosis technology, is how to effectively treat these brines so that they do not pose an environmental risk. The traditional methods for disposing of the RO concentrate have been surface water discharge, deep well injection, evaporation ponds, and land application ((AWWA) Membrane Residuals Management Subcommittee 2004). It is becoming clearer that these conventional methods are not sufficient when considering the tightening environmental regulations and limitations on discharges. Peréz-Gonzáles et al. (2012) present possible treatment technologies for reverse osmosis concentrates. The technologies have been categorised according to the sources of the RO retentate and the maturity of the technology. There are three different sources of retentate recognised: desalination plants, tertiary processes in wastewater treatment plants, and mining industries. (Pérez-González et al. 2012) The third class mentioned is the one focused on in this study.

The hypersaline brines produced in industrial and mining operations cause constantly expanding environmental problems around the world, because of the exponential increase in their volumes. (Randall et al. 2011) There have been considerable efforts made towards reaching the goal of Zero Liquid Discharge (ZLD) or near-ZLD by further treating the retentate from RO. The selection of the best available technology (BAT) depends on several variables. Figure 7 shows the conceptualisation of the steps to be taken in order to reach this objective. The usual approaches have been based on the use membrane and

thermal methods or a combination of these. Before the use of any of these technologies, attention needs to be paid to pre-treatment methods needed for each of them. (Subramani, Jacangelo 2014)

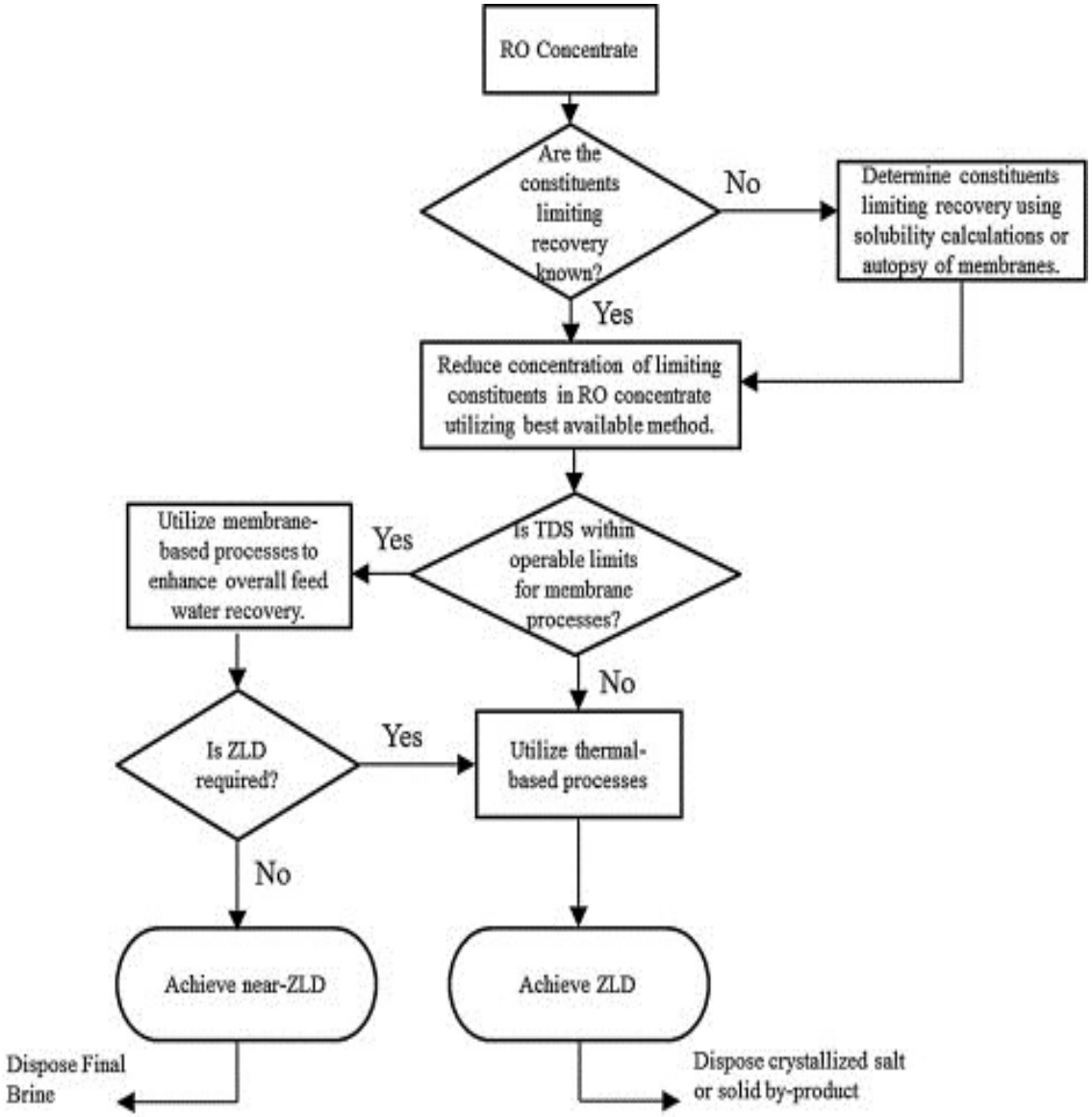

Figure 7. The steps required in achieving near-ZLD or ZLD of retentate from RO processes (Subramani, Jacangelo 2014).

5.2 Membrane methods

Forward osmosis

Forward osmosis like RO is an osmotic process. The difference between them is that FO utilizes the osmotic pressure differential across the membrane as a driving force for transporting water across the membrane while RO uses the hydraulic pressure differential, as was presented earlier. The outcome of FO is that a concentrated feed stream is formed while a very concentrated stream called draw solution is diluted. (Cath et al. 2006)

The most important advantages of FO are that it is operated at low or no hydraulic pressures, it has the capability to reject a large range of contaminants, and its membrane-fouling tendency can be lower than that of pressure-driven membrane processes. Due to the fact that the only pressure required in the process results from flow resistance in the membrane module, the equipment needed for FO is quite simple and also the membrane support is a smaller problem. (Cath et al. 2006)

FO is, at the moment, not as well-known and used in water treatment applications as RO. Still, FO has been utilized in treating industrial wastewaters at bench-scale, in concentrating landfill leachate at both pilot- and full-scale, and in treating liquid foods in food industry at bench-scale. There exist also other applications, in which the use of FO is being examined. (Cath et al. 2006) Lately increasing attention has been directed towards technology options that utilise forward osmosis (FO) for the treatment of RO retentate.

Electrodialysis

Equation 5 presents the overall reaction of electrochemical decomposition of sodium sulphate. This reaction relies on the anodic and cationic reactions, which occur according to equations 6 and 7, respectively. In order to produce a solution of sodium hydroxide and sulphuric acid the prevention of reverse reaction between H^+ and OH^- is needed. This is possible using a cathode made out of mercury or alternatively a diaphragm cell.

$$2\,Na_2SO_4 + 6\,H_2O \rightarrow 2\,H_2SO_4 + 4\,NaOH + 2\,H_2 + O_2 \quad (5)$$

$$2\,H_2O \rightarrow 4\,e^- + 4\,H^+ + O_2 \quad (6)$$

$$2\,H_2O \rightarrow 2\,e^- \rightarrow 2\,OH^- + H_2 \quad (7)$$

Electrodialysis is an electrochemical method relying on cation- and anion-selective ion-exchange membranes. The decomposition of sodium sulphate using electro dialysis is carried out using a cell that is divided into three sections or cells by a cation-exchange membrane (CM) and an anion-exchange membrane (AM). The principle is that the sulphate solution flows through section in the middle and the sodium and sulphate ions are transported through CM and AM, respectively. In the cathode section, sodium hydroxide and hydrogen, and in the anode section sulphuric acid and oxygen, are formed. With this method, sulphuric acid of 5 – 15 w-% and sodium hydroxide of 15 – 20 w-% can be reached. The energy consumption related to this method is 3500 – 4000 kWh/t NaOH and the current efficiency is between 60 and 80 percent. The electrical energy consumption can be decreased using H_2 and O_2 reaction gases in a fuel cell. Alternatively, the electrodialysis cells can be used with gas-diffusion electrodes. The use of further developed anion-exchange membranes consisting of styrene – divinylbenzene copolymer improves current efficiencies and enables the recovery of more concentrated products. (von Plessen 2000) Figure 8 depicts the principle of electrodialysis.

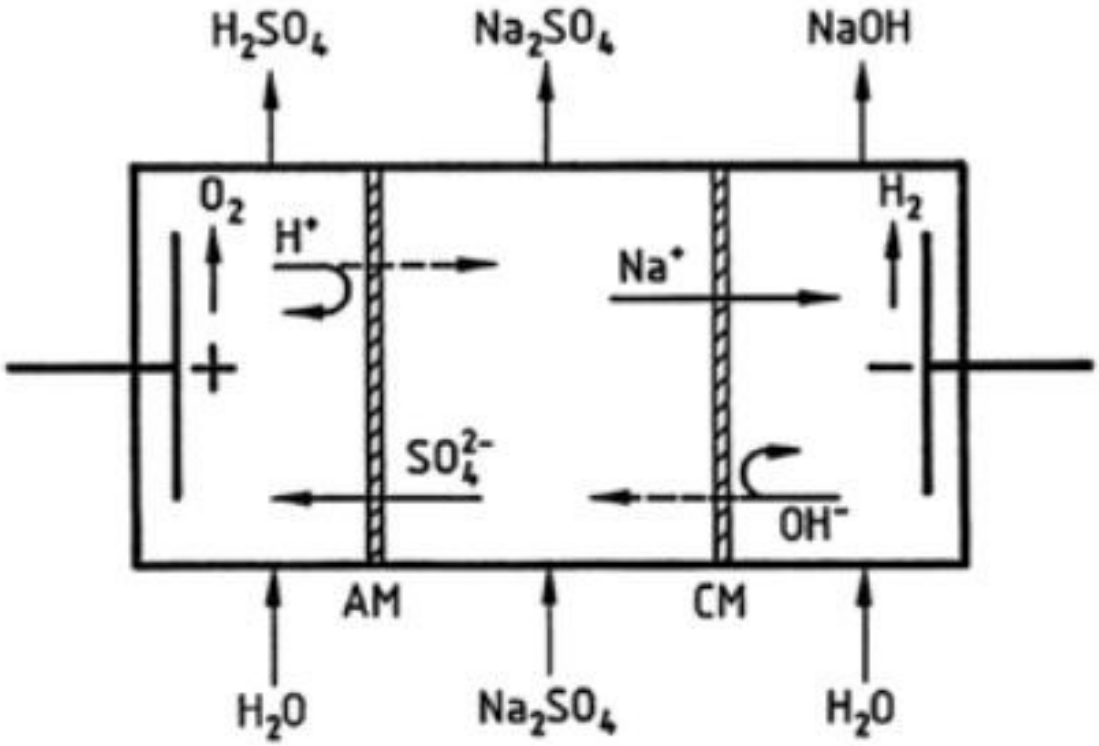

Figure 8. The principle of decomposing sodium sulphate electrolysis using electrodialysis (von Plessen 2000).

Bipolar membrane electrodialysis

As a viable option for the treatment of RO retentates with high salinity, bipolar membrane electrolysis (BMED) has been suggested. BMED is a membrane technology, with which it is possible to produce acids and bases from the corresponding salts present in the brine. (Ibáñez et al. 2013) This process includes mono-polar cation- and anion-exchange membranes, which are set up in conjunction with bipolar membranes in alternating series. This installation is influenced by an electrical potential gradient. The principle of BMED is shown in Figure 9. The formation of a typical BMED stack is three cells, two mono-polar membranes and a bipolar membrane. This stack is repeated in the system. The salt solution is within the cell between the mono-polar membranes and acid and base solutions are in the cells between mono-polar and bipolar membranes. By applying an electrical potential gradient across a repeating unit, an acid and a base are formed. This happens, when the protons, formed in the bipolar membrane, react with the anions gained

from the salt solution, producing an acid. Correspondingly, the base is produced by hydroxides and cations. (Strathmann 2010)

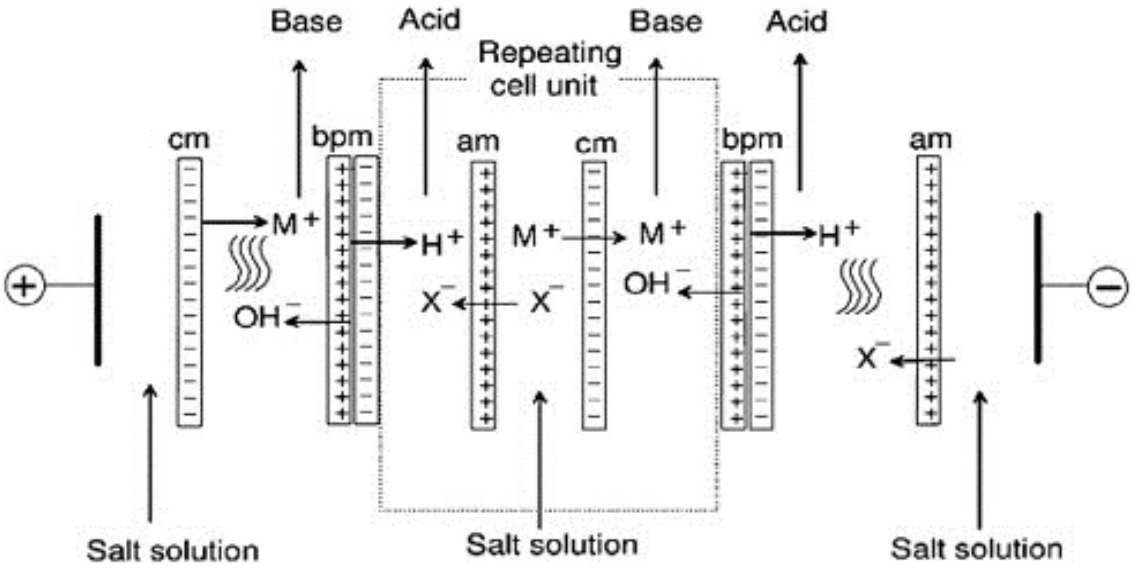

Figure 9. A schematic drawing of the principle of BMED (Strathmann 2010).

The costs of BMED are divided into investment related and operating costs. It is worth noting that concentration polarization effects typically do not limit this value in the case of BMED. In the unit cell, the most expensive component is the bipolar membrane, which also has a limited working time, as does the anion-exchange membrane. Thus, the investment cost is mostly determined by the stack component costs. The operating costs are caused mainly by the energy requirements that come from two sources. The first is the energy needed for the dissociation of water in the bipolar membrane. The other is energy needed for transferring of the salt ions originating from the feed solution, and protons and hydroxide ions that come from the transition region of the bipolar membrane ending up in the acid and base solutions. (Strathmann 2010) The cost structure of BMED method can be seen in Figure 10.

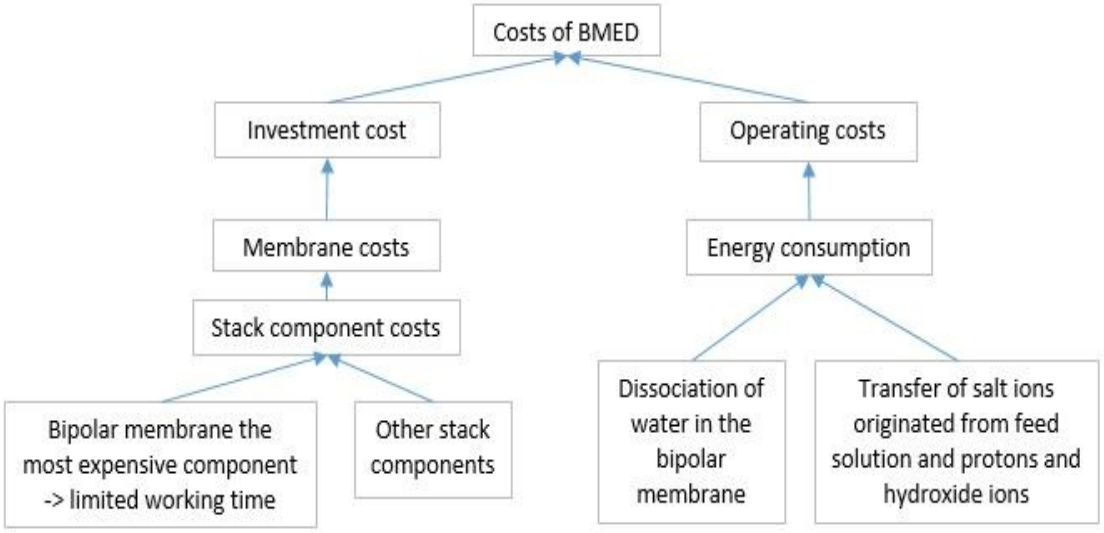

Figure 10. The costs of bipolar membrane electrodialysis.

The economic restrictions on the use of BMED emerge from the limitations on stability of ion-exchange membranes when used with strong acids and bases, and the need for costly bipolar membranes. A technical problem of this technology is the precipitation of multi-valent ions in the flow stream of a bipolar membrane stack that contains the base. To address this problem, comprehensive pre-treatment of the feed solution is required. Still most problematic is often the product contamination by salt ions that permeate the bipolar membrane. (Strathmann 2010)

This technology has already gained results demonstrating its usability in numerous applications. Some commercial applications exist already, for example, BMED is used in recovering organic acids from fermentation. In addition, there are many applications at pilot plant stage and the largest part of them are still in laboratory test stage. (Ibáñez et al. 2013) The production of acids and bases from RO retentates has not been studied very extensively. Based on the results of laboratory scale testing of the treatment of RO retentate by Badruzzaman et al. (2009) BMED can be determined technically feasible in the production of 0.2 M acid and base. Ibáñez et al. (2013) have tested this technology in a bench scale setup for model RO retentates from seawater desalination processes. The

results suggest that the BMED technology could provide a viable option for the production of acids and bases from RO retentates assuming that appropriate pre-treatment methods are used. (Ibáñez et al. 2013)

5.3 Biological methods

Biological methods for sulphate removal are based on the biochemistry of a range of microbial communities. Energy generation by microbes requires the transfer of electrons from electron-rich (reduced) substrates that can be organic matter, hydrogen carbon monoxide, etc. to electron-deficient (oxidized) species that can be i.e., oxygen or sulphate. The microbial use of sulphate as an oxidising agent in addition to the reduction of it into hydrogen sulphide (HS^-) form the basis for biological sulphate removal methods. Biological sulphate removal consists of two stages. The first of these is the dissimilatory sulphate reduction, which is carried out by sulphate reducing bacteria (SRB). Sulphide, which is produced in the previous stage, is in the second stage oxidized into elemental sulphur. This is done either by chemotrophs, which are colourless sulphur bacteria, or by phototrophs, which are purple and green sulphur bacteria. (INAP: International Network for Acid Prevention 2003)

When the conditions are limited by oxygen, $O_2 < 0.1$ mg/l, the main product in the sulphide oxidation step is elemental sulphur, but in the case of sulphide-limited conditions sulphate is formed. Options for the removal of sulphide after the first step are precipitation of metal sulphides (MeS) or by hydrogen sulphide (H_2S) stripping. The latter is used in wetlands and bioreactors. (INAP: International Network for Acid Prevention 2003)

Bioreactor

Several aspects need to be considered when it comes to the use of bioreactors in sulphate removal. The main issues are related to the substrates used, the toxicity effects of the waste stream on SRB, and which bioreactor design is used. Simple organic compounds are the favoured substrates for SRB, and the more complicated organic compounds, for

example molasses, are left to be oxidized by other anaerobic bacteria. (INAP: International Network for Acid Prevention 2003) The deciding factors in the competition between SRB and other anaerobic bacteria over the substrate available is the ratio of chemical oxidation demand (COD) and sulphate concentration of the wastewater (Hulshoff Pol et al. 1998).

There are also other limiting factors on anaerobic treatment of sulphate than the aspects related to substrate utilisation. Due to the hydrogen sulphide (H_2S) formation in anaerobic conditions, biological methods for sulphate removal have not always been considered as the more preferable options. One reason is the toxicity of H_2S on many bacteria when present in higher concentrations. If H_2S is allowed to accumulate in the system, it can cause considerable inhibition and in the worst case, it can lead to complete process failure. Another factor that can cause anaerobic bacteria inhibition is high cation (Na^+ and Ca^{2+}) concentrations. In concentrations above 400 mg/l Ca^{2+}, considerable scaling of biomass by Ca-precipitates may happen. The occurrence of clogging problems caused by precipitates in the piping system are also possible. (Hulshoff Pol et al. 1998)

There are many different types of bioreactors in use. They include, for example, mixed, packed bed, fluidized bed, sludge blanket, and gas-lift reactors. An example of biological sulphate removal technology that uses bioreactor is SULFATEQ by PAQUES. (INAP: International Network for Acid Prevention 2003) According to Silva et al. (2012) studies conducted on sulphate removal using bioreactors have been on waters with the maximum of 2.0 kg of SO_4^{2-}/m^3 d. Therefore, this method can be considered best suited for low or moderate sulphate loadings. (Silva et al. 2012)

Membrane bioreactor

Membrane bioreactor (MBR) is a technology, which utilises membrane filtration in conjunction with biological methods. Usually, low-pressure membrane filtration is used, namely microfiltration or ultrafiltration, in order to retain the liquor mix found in the bioreactor. The product of MBR is treated particle-free effluent. (Drioli, Macedonio 2012)

MBR allows the avoidance of the problems associated with the sedimentation tank and biological treatment stages (Visvanathan et al. 2000). MBR has many advantages comparing to traditional bioremediation. The effluent recovered using MBR is of high quality and nearly free of suspended solids. It also enables partial disinfection without using chemicals. Sludge production is reduced. These are just to name a few. (Drioli, Macedonio 2012)

However, there are serious risks of biofouling related to MBR and the system requires considerable pumping energy to recirculate wastewater through membrane modules. In addition, MBR systems are quite sensitive to temperature, which can cause problems when operating in colder environments. (Mortazavi 2008, pp. 58) In terms of costs, MBR is considered to have higher initial investment costs than traditional treatment methods. Most of the operating costs come from coping with membrane fouling. (Drioli, Macedonio 2012)

5.4 Precipitation methods

Ion exchange

Ion exchange is a process, which relies on the exchange of ions or molecules between solid and liquid. There are no considerable changes in the solid structure of the resin. The resins used in ion exchange are large polar exchange groups containing materials that are in the form of three-dimensional networks. The mechanism is that one of the ions targeted is removed from the liquid stage by attaching it to the solid state in exchange for another ion that is released into the solution. These ions released into the solution are often hydrogen (H^+) or hydroxyl (OH^-) ions. When removing anions, they would be attached to the positively charged resin, called anionic resin, and for the removal of cations, negatively charged resin is used, called cationic resin. The resins are regenerated by reverse reaction of washing the cationic and anionic resins in acid or sodium hydroxide solution, respectively. (Bowell 2004)

As is the case with RO, in systems, where Ca_2SO_4 is present, there is considerable risk of scaling in traditional ion exchange circuits. A technology option for the removal of sulphate from water containing $CaSO_4$ is the GYP-CIX process. This technology differs from conventional ion exchange technologies by using resins that can be regenerated with low cost reagents such as lime and sulphuric acid. The design of the resins is such that it targets calcium and sulphate, which leads to considerable reduction in gypsum in the effluent and therefore, lowering of the total dissolved solids (TDS) and corrosion potential. This technology has been tested in pilot plant level in South Africa, where the results indicate that the problem of gypsum precipitation can be significantly reduced with the use of GYP-CIX process. GYP-CIX process is suitable for solutions with sulphate concentration up to 2000 mg/l and calcium concentration up to 1000 mg/l. Above these concentration levels membrane filtration is needed in order to remove salts. (Bowell 2004, INAP: International Network for Acid Prevention 2003)

Lime and limestone precipitation

The use of hydrated lime ($Ca(OH)_2$) and limestone ($CaCO_3$) in the precipitation of gypsum ($CaSO_4 \cdot H_2O$) is commonly used in mining operations for neutralization. However, this method can also be applied to remove sulphates from mine waters. The precipitation reactions are seen in Equations (8) and (9), in acidic and alkaline conditions, respectively. This addition of lime raises the pH value of the solution. The amount of separable sulphate by this method is limited by the solubility of gypsum, which varies according to composition and ionic strength between 1500 – 2000 mg/l. This limitation on sulphate removal points to this process being possibly more suited as a pre-treatment stage of the RO retentate treatment. (Fajtl et al. 2002, INAP: International Network for Acid Prevention 2003)

$$CaCO_3(s) + H_2SO_4 + H_2O \leftrightarrow CaSO_4 \cdot 2H_2O(s) + CO_2(g) \qquad (pH<7) \qquad (8)$$

$$CaCO_3(s) + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O(s) + CO_3^{2-} \qquad (pH>7) \qquad (9)$$

Barium salt precipitation

There are also other chemicals used in mine waters. Barium salts can be used to reduce sulphate loads because of the highly insoluble character of barium sulphate ($BaSO_4$). Typically used barium salts in sulphate removal are barium hydroxide ($Ba(OH)_2$), barium carbonate ($BaCO_3$), and barium sulphide (BaS). The precipitation reactions are listed below (Equations 10 – 12). The use of barium hydroxide and sulphide is not limited by pH, where as barium carbonate has limited applicability in neutral to strongly alkaline and in strongly acidic pH levels. It is also possible to modify this method to also remove dissolved metals. (INAP: International Network for Acid Prevention 2003)

$$BaCO_3(s) + H_2SO_4 \rightarrow BaSO_4(s) + H_2CO_3 \quad (10)$$

$$Ba(OH)_2(s) + H_2SO_4 \rightarrow BaSO_4(s) + 2H_2O \quad (11)$$

$$BaS(s) + H_2SO_4 \rightarrow BaSO_4(s) + H_2S \quad (12)$$

A comparison of the effectivity of different barium salts and lime used in the removal of sulphates from effluent in different pH levels can be seen in Table 7. From the these results it seems clear that the use of $Ba(OH)_2$ would yield the best results in all the pH levels tested. (Bowell 2004) The optimal pH level for all of these salt precipitation options would be expected to be near neutral, or a bit above.

Table 7. The effectivity of Ba- and Ca-salt precipitation in sulphate removal (% removal) (Bowell 2004).

pH	Lime	$BaCO_3$	BaS	$Ba(OH)_2$
2.9	62.3	24.2	95.6	107.7
7.9	80.5	101.6	110.8	137
12	51	90.1	90.1	134

Because barium salts are quite expensive, recycling of the formed barium sulphate sludge is needed. An example of this type of a configuration is a system where barium sulphide is fed into a reactor/clarifier with the sulphate containing water, where the pH level is kept constant. The formed barium sulphate in the bottom of the clarifier is collected and from it, barium sulphide is regenerated using thermal reduction and fed back to the precipitation stage of the process. The hydrogen sulphide (H_2S) also produced in the reduction can be led to an air stripper and converted into elemental sulphur with the use of sulphide oxidizer. (INAP: International Network for Acid Prevention 2003, pp. 3-2 – 3-3) Problematic with the utilisation of barium salts as precipitating agents is that these compounds are toxic, and as such are more dangerous as sulphates (Silva et al. 2012). Their release into the environment can cause serious problems. Their utilisation also requires a new chemical being approved for usage on the mine site.

Ettringite precipitation

A much used method for sulphate removal from AMD is precipitation of ettringite ($3CaO \cdot CaSO_4 \cdot Al_2O_3 \cdot H_2O$), a hydrous calcium sulphate mineral. Ettringite is a colourless or yellow mineral that crystallises in the trigonal system. There is also a commercial process for sulphate removal presented here, which is based on ettringite precipitation and its recycling. This is the SAVMIN process. (INAP: International Network for Acid Prevention 2003, pp. 3-1 – 3-6)

Janneck et al. (2012) have tested the ettringite process in a laboratory scale. This was done by first raising the pH of the acidic mine effluent to the value pH = 10 using lime treatment. After this stage, the metal containing sludge was removed with the use of filtration. The sulphate content of the remaining filtrate had reduced from the original 3900 mg/l to 2900 mg/l and it was used for ettringite precipitation. Because the pH level required for the precipitation ranges between 11.0 – 11.5, another dose of lime was found necessary before the addition of an aluminium source. The remaining sulphate content in the treated water in addition to the amount of the reagent needed are affected by the aluminium source quality. Based on screening test conducted on different aluminium sources, it was

discovered that the all tested reagents in the liquid form suited well for the precipitation of ettringite. The same has not been discovered of solid form reagents. Of them, the ones based on crystalline aluminium hydroxide (Hydrargilite) have been found not suitable for ettringite precipitation even in relatively large doses. However, aluminium hydroxide, in its freshly precipitated form as a gel with an amorphous form, is used in the SAVMIN process. (Janneck et al. 2012)

The SAVMIN process is based on successive stages, where dissolved sulphate is extracted from ARD water by precipitation. The first stage consists of addition of lime in order to reach a pH level around 12. The precipitation of metals and magnesium happens as hydroxides. This stage is followed by the seeding of the water with gypsum crystals, which leads to the catalysing of the precipitation of gypsum from the supersaturated solution. Part of the formed gypsum precipitate is recycled back to the feed water as seed crystals, and the rest is discarded. Third stage is the addition of aluminium hydroxide, which causes the precipitation of ettringite. At the same time, calcium and sulphate are both removed. The required pH level is sustained by adding lime. Filtration and thickening are used to extract the formed ettringite slurry from the feed water. The fourth stage consists of treating the waste water stream with CO_2 in order to lower the pH level. The precipitation and extraction of comparatively pure $CaCO_3$ is carried out using filtration. Ettringite slurry is decomposed and using sulphuric acid for the purpose of regenerating aluminium hydroxide for reuse in the third stage. (INAP: International Network for Acid Prevention 2003, pp. 3-4 – 3-5) The aspect of regenerating and recycling of aluminium hydroxide enhance the feasibility of this process. Results gained from the use of this process in a demonstration plant in a South African gold mine seem promising regarding the sulphate and dissolved metal removal capabilities of the process (INAP: International Network for Acid Prevention 2003, pp. 3-4 – 3-5). The flowsheet of SAVMIN process is presented in Figure 11.

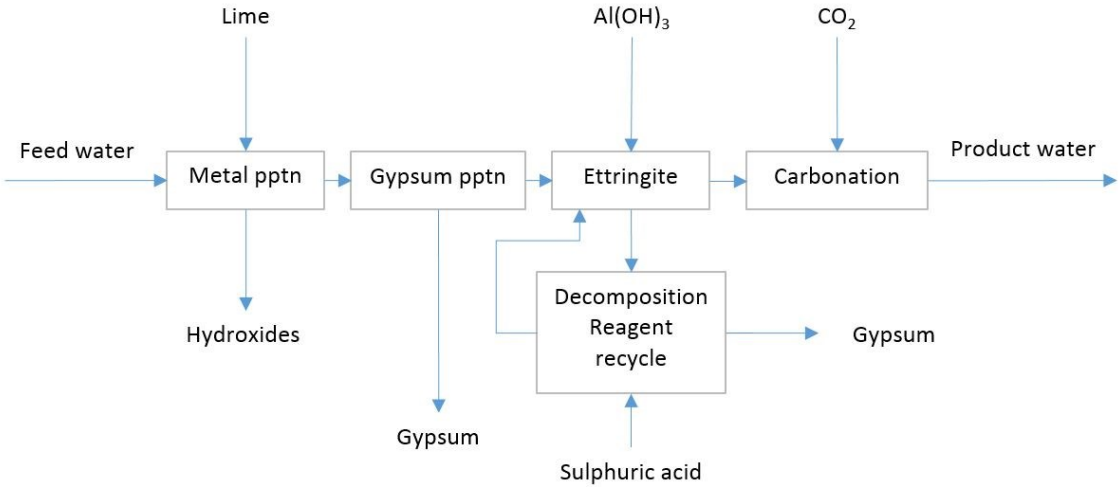

Figure 11. Flowsheet of the SAVMIN process (Adapted from: INAP: International Network for Acid Prevention 2003).

There are also other commercialised processes, which utilise ettringite precipitation. One of these is Outotec Ettringite process. It differs from the SAVMIN process quite clearly as can be seen in Figure 12. The first process stage is the precipitation of ettringite, which is carried out at pH level 11 – 13 with lime milk ($Ca(OH)_2$) and aluminium. This stage can be preceded by gypsum precipitation if needed. The ettringite precipitation stage is followed by final neutralisation conducted with carbon dioxide. The process can be applied for the removal of sulphate from gypsum-saturated waters. Furthermore, it is suitable for the precipitation of sulphate when it is associated with sodium and potassium sulphates, which are highly soluble. The sulphate concentration reached with this process has been reported to be 200 – 1000 mg/l. In addition to the sulphate precipitation the process also includes the removal of metal impurities as hydroxides as is the case with the previously presented process concept. The end products of the Outotec Ettringite process are the treated water with low sulphate content and a stable and solid precipitate that possesses high buffer capacity. (Anonymous A 2016)

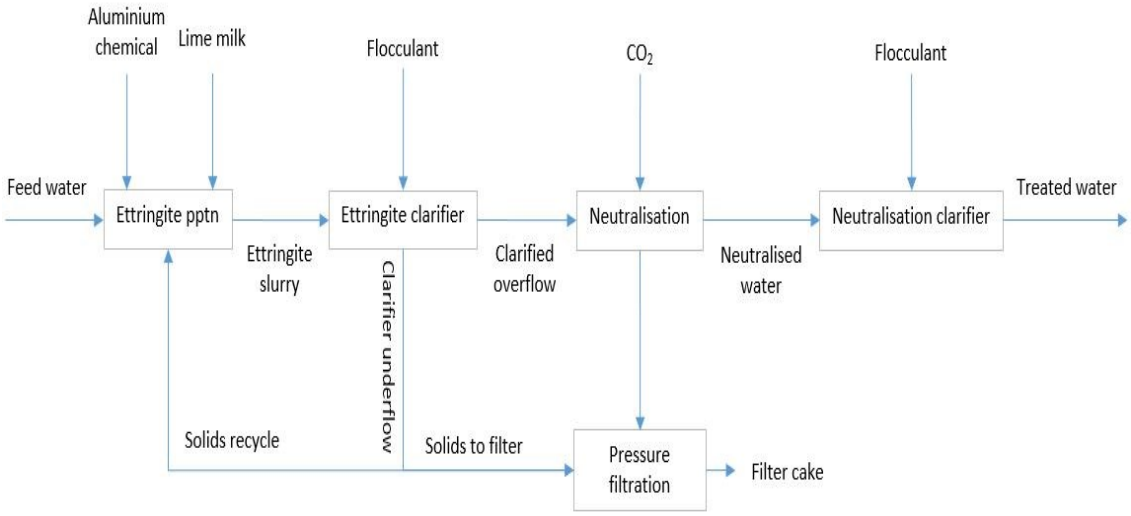

Figure 12. Flowsheet of the Outotec Ettringite process (Adapted from: Anonymous A 2016)

Jarosite precipitation

One option is also to precipitate the sodium out of the solution as natro-jarosite ($Na[Fe_3(SO_4)_2(OH)_2]$. The use of precipitation of jarosite compounds is already common in zinc industry, where it is used to get rid of iron found solubilized in the processing circuit (Dutrizac 1999). Jarosites are crystalline iron(III) sulphate oxide hydrates with extremely low solubility. (Wendt et al. 2000) The process of removing iron using jarosite precipitation has been used for several decades, so the technology is mature. Shengfeng et al. (2007) have studied using the method of natro-jarosite precipitation as way of treating wastewater with high sulfur-concentration. Because jarosite's indissolubility in thin acids and ease of deposition, washing, and filtering, the removal of Fe^{3+} from the solution is simple. The process requires certain temperature, acidity, and the presence of ammonium or alternatively alkaline metal cations. (Shengfeng et al. 2007)

The formation reaction for jarosite can be seen in equation 13, where Na^+ ion can be replaced for example with potassium (K^+) or ammonium (NH_4^+) ion, and the iron(III) (Fe^{3+}) ion can be replaced by aluminium (Al^{3+}), gallium (Ga^{3+}) or chromium (Cr^{3+}).

(Shengfeng et al. 2007) There is, however, another reaction in competition with the formation of natro-jarosite: the formation goethite (Equation 14) (Casas et al. 2007).

$$3Fe^{3+}(aq) + 2SO_4^{2-}(aq) + M^{+}(aq) + 6H_2O(l) \rightarrow MFe_3(SO_4)_2(OH)_6(s) + 6H^{+}(aq) \quad (13)$$

$$Fe^{3+}(aq) + H_2O(l) \rightarrow FeOOH(s) + 3H^{+}(aq) \quad (14)$$

Which of these formation reactions is the predominant one, is determined by the composition of the solution and temperature. The solubility of both natro-jarosite and goethite depend on the ionic equilibrium of bisulphate and sulphate complexes in addition to species like HSO_4^- and H^+. The concentrations of these species in turn are depend considerably on acidity and temperature, and finally determined by specific reaction equilibriums. In order to control the formation of these compounds, it is essential to have precise thermochemical data of these reactions at the temperature in question. (Casas et al. 2007) The effects of temperature and pH on jarosite precipitation and stability can be seen in Figure 13. From it can be seen that the pH range is quite limited, below 4, and it shifts to lower pH values when the temperature rises. This raises questions about how to handle and store the formed jarosite precipitate.

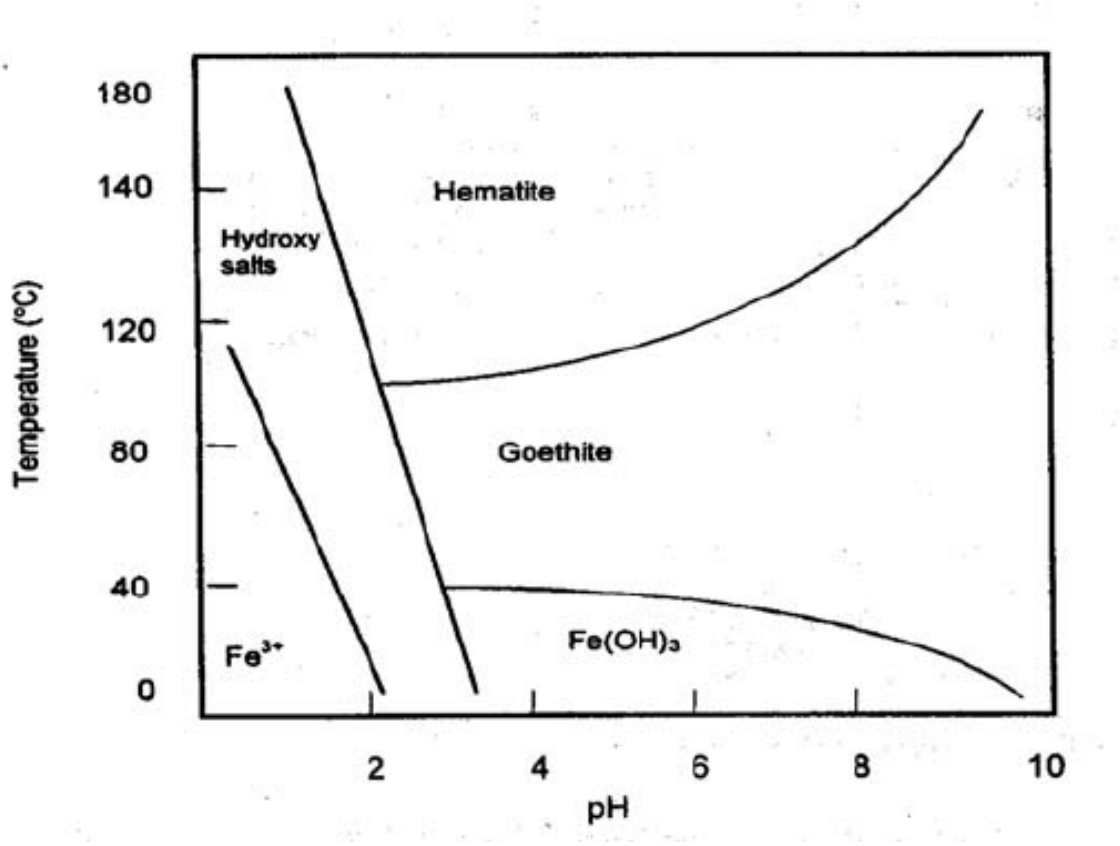

Figure 13. The effect of temperature and the pH of the solution on the precipitation and stability of different iron precipitates from 0.5 M ferric sulphate solutions. The jarosite compounds are included in Hydoxy salts. (Svens 2012)

Shengfeng et al. (2007) report that the optimal pH level for the formation of jarosite precipitation has been found to be between 2.0 – 3.0 at room temperature and 1.0 – 2.3 at 100 °C. At pH level above 3.2, the precipitation of Fe^{3+} as $Fe(OH)_3$ is increased, which decreases the amount of sulphates removed. (Shengfeng et al. 2007)

There has already been speculation that the formation of natro-jarosite could have its uses in leaching operations using waters with high salinity including considerable concentrations of sodium (Casas et al. 2007), which makes this treatment option an interesting one to consider for the treatment of the retentate in this study. This technology option, however, does not include the regeneration and recycling of chemicals. The formed natro-jarosite is considered an insoluble compound limiting the options for

utilisation. There are not many uses found for jarosite in literature. Most often, it is disposed of as solid waste. One possible option would be to recycle some of the formed jarosite as seed crystals back to the precipitation process.

Hydrotalchite precipitation

Hydrotalcites are layers of mixed metal hydroxide layers with a positive charge, which are separated by interlayer water molecules in addition to exchangeable anions. Their general formula is $M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2A^{n-}y\ H_2O$. In the formula M^{2+} and M^{3+} represent divalent and trivalent metal ions, respectively, *x* determines the proportion of trivalent metal ions, *A* denotes an anion with a negative charge of *n*, and *y* tells the amount of H_2O between the layers. The usual ratio of M^{2+} and M^{3+} in hydrotalcites is between 2:1 and 3:1. The formation of these compounds is generally by co-precipitation of solutions of divalent (such as Mg^{2+} and Fe^{2+}) and trivalent (such as Al^{3+} and Fe^{3+}) metal cations. Suitable pH range for this process is from neutral to high. The suitability of a range of different cations (e g., Ni, Zn, Mn, Ca, Cr, La) and anions (e.g., SO_4^{2-}, HCO_3^-, CrO_4^{2-}, UO_2^{2+}) being substituted in the structure of hydrotalcite in the case of *in-situ* formation, make this a potential option for the treatment of mine water and other waste waters. Other benefits have also been determined. These include the rapid nature of the formation kinetics, entrainment of particulate or colloidal material in conjunction with *in-situ* formation, and also the option for reaching additional stabilisation by adding silica between layers or by calcination in order to form a spinel. (Douglas et al. 2014, Douglas 2014)

5.5 Thermal processes

Evaporation: Brine concentrators and crystallisers

A much used treatment method for the retentate is evaporation either in ponds or in evaporation units, which aim at reducing the water content in the solution further, i.e. concentrating the retentate further. When the goal is to process the retentate all the way to dry salts, this method becomes a ZLD option. For the use of evaporation, a considerable

capital investment is required. It is also worth noting that evaporation has a high energy consumption and the possible disposal costs of the formed salt or brine together can cause huge operating expenses. However, an upside to using evaporation after an RO system is that it enables greater product water recovery because of the high-purity distillate gained from the RO retentate. Two systems suitable for the treatment of RO retentate, which rely on evaporation presented here are brine concentrator and crystalliser. (Mickley 2006, pp. 209) These methods are in use, for example, in power generation industry (Howe et al. 2012, pp. 335).

Brine concentrator, also known as a vapour compression evaporator system, resembles a conventional single-state evaporator with the difference that a compressor is used to compress the vapour released from the boiling solution (Mickley 2006, pp. 211 – 214). This equipment consists of bundles of vertical tubes, in which the evaporation of the RO retentate takes place from a thin film located on the walls inside the tubes. The idea is that the concentrators compress the vapour coming from the heated concentrate, while the pressurized steam can be reused in the heating of the RO retentate coming in. Heat from condensing water vapour, which is on the outside of the tubes, is absorbed by the retentate. The latent heat of vaporisation is conveyed from the water vapour through the wall of the tube and to the thin film of the brine found inside the tube. Further use of the stream is possible by returning it after the heat exchange back to the membrane treatment process. In order to prevent scaling of the heat transfer surface, calcium sulphate is often added to the recycle to provide nucleation sites for scale precipitation. (Subramani, Jacangelo 2014) This seeded slurry process enables the concentration of the retentate by 97.6 percent without the development of scaling problems in the evaporator. If brine concentrators are used together with crystallizers or spray towers, ZLD can be reached in any climate conditions. There were approximately a dozen brine concentrators used in the treatment of retentate from industrial RO plants in 2006. The experiences from these systems have indicated that brine concentrators are viable options for these applications and that they are very reliable solutions. (Mickley 2006, pp. 211 – 214) A brine concentrator set up can be seen in Figure 14.

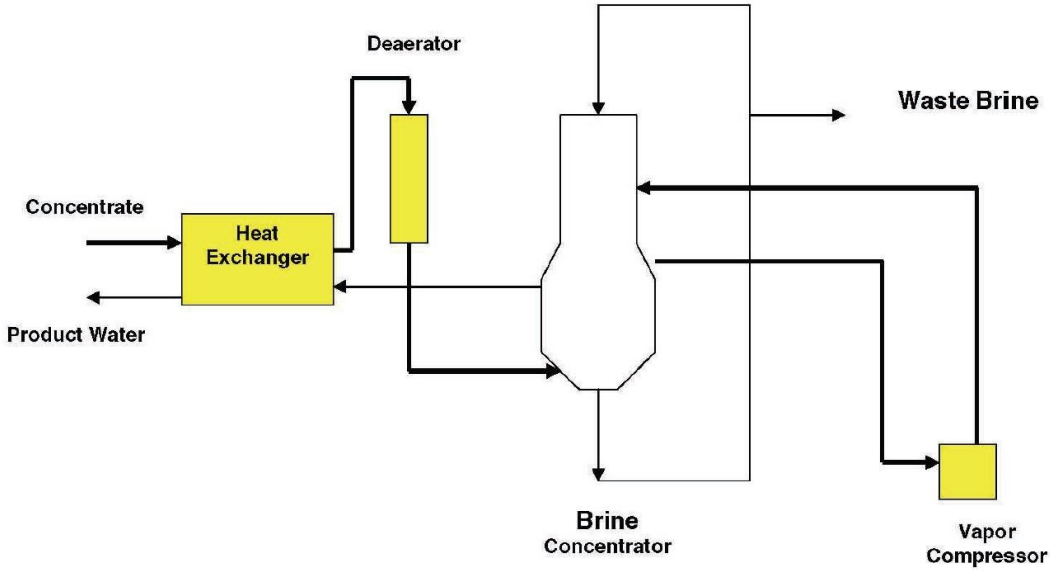

Figure 14. A schematic of a brine concentrator system (Mickley 2006, pp. 213).

Crystallisers have been used for years for the concentration of feed streams in industrial processes, and recently the use of crystallisers has increased also in the concentration of retentates from desalination processes, like the previously presented brine concentrate evaporators. The use of crystalliser technology makes most sense in applications, in which the cost of construction of solar evaporation pond would be very high, the solar evaporation rates are negative, or deep well disposal is not an option. (Mickley 2006, pp. 214 – 216)

Evaporative crystallisation differs from previously presented concentration by evaporation, because instead of merely increasing the concentration of the dissolved solid compound it aims to recover the compound in essentially pure form and completely free of the solvent. This method is suitable for the recovery of salts whose solubility is only somewhat temperature dependant. The steps in an evaporative crystallisation process can be seen in Figure 15. (Billet 2000)

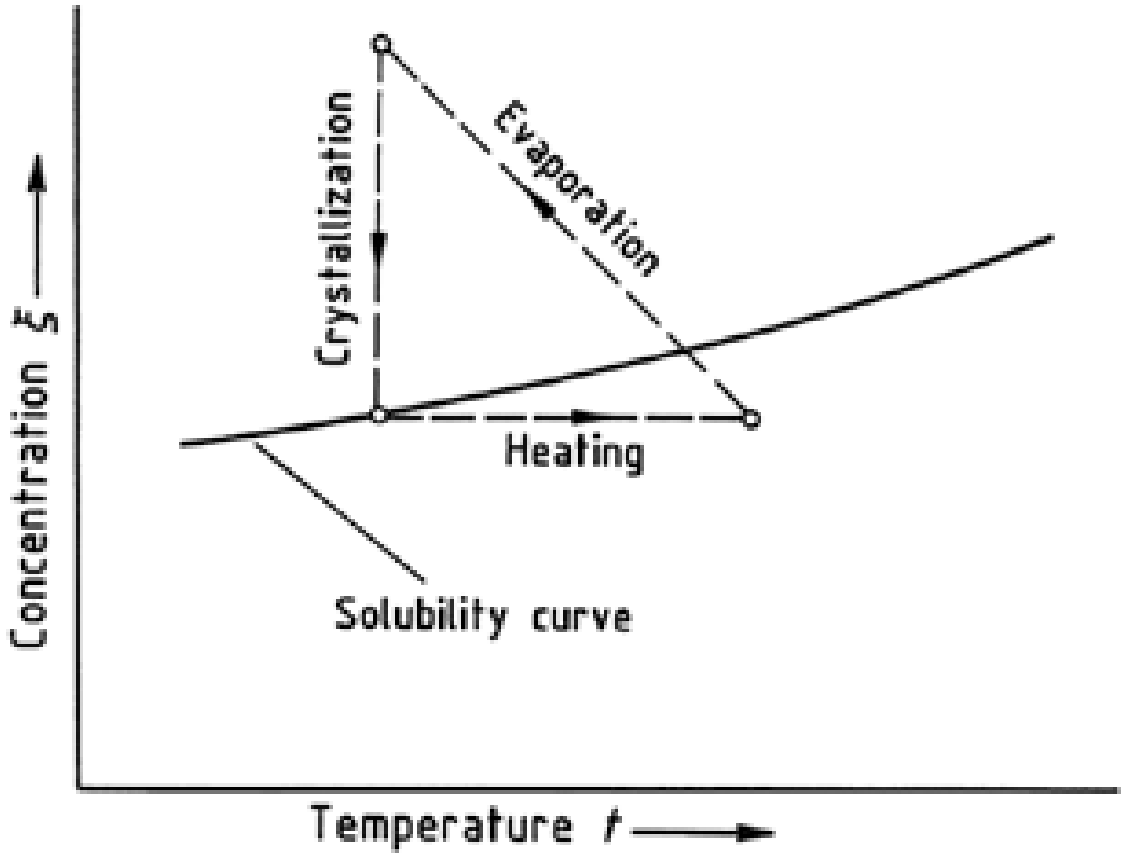

Figure 15. Steps of evaporative crystallisation process (Billet 2000).

A unit of brine crystalliser consist of vertical cylindrical vessels with a heat input from either vapour compressors or an already available steam supply. The latter option is the more economical of the two for smaller systems. For larger systems, the former manner of heat supply is preferred. (Mickley 2006, pp. 214 – 216) Figure 16 depicts a vapour compression crystallisation system.

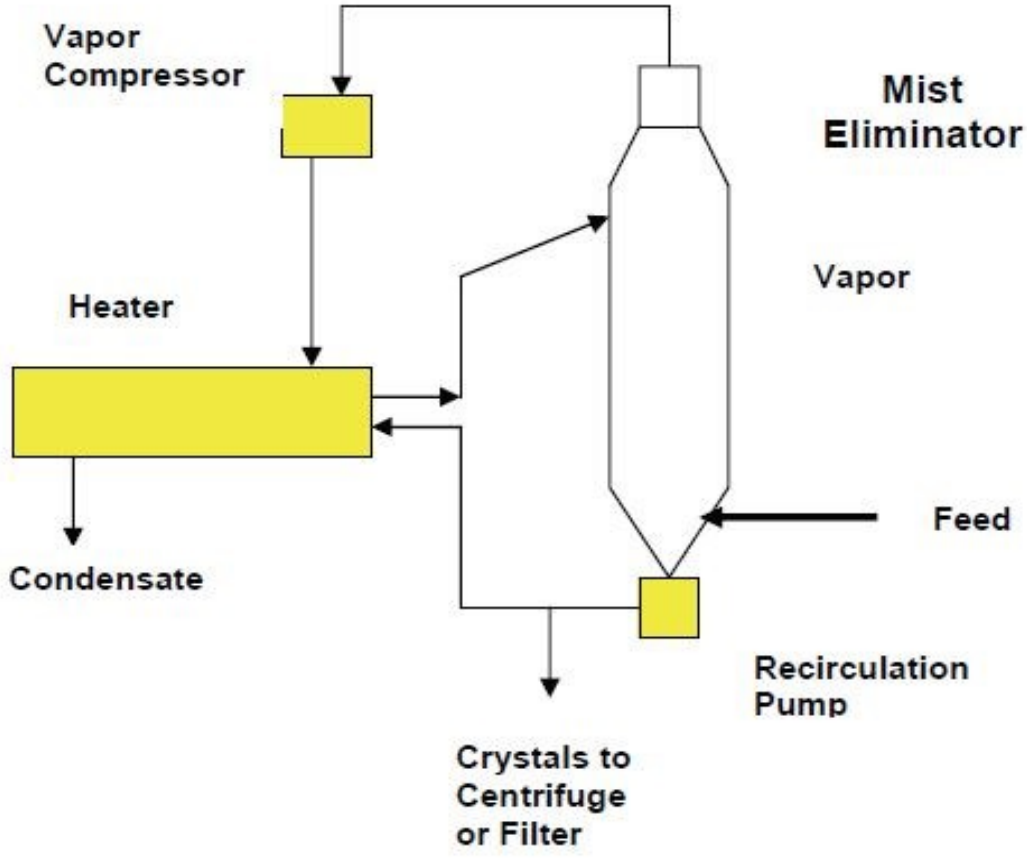

Figure 16. A schematic of a forced circulation vapour compression crystallization system (Mickley 2006, pp. 215)

A typical model used is forced circulation (FC), in which the size and distribution of crystals is determined by temperature in the heat exchanger, cooling water flow rate, design of the vessel, rate of vaporisation, and residence time. (Farahbod et al. 2012) Farahbod et al. (2012) have studied the effectivity of FC evaporators as crystallising evaporators for saline solutions. This was tested by mixing RO retentate with recirculating brine and pumping the mix into a shell-and-tube heat exchanger, where vapour from the compressor was used to heat the brine. The salts were able to be precipitated from the solution, after being concentrated due to the evaporated water. (Farahbod et al. 2012)

It is clear that both brine concentrator and crystalliser technologies are well developed. On the other hand, because they are often used together, considerable energy consumption (65 – 80 kWh/m^3) is related to their usage. In addition, a drawback from implementing these methods is that the equipment required are relatively large and complex. (Subramani, Jacangelo 2014)

Carbothermic reduction of sodium sulphate

Another solution could be reducing sodium sulphate (Na_2SO_4) back to sodium sulphide using coke (Equation 15) (Erdemoğlu et al. 2006). Sodium sulphide can then be recycled back into the process. The utilization of this method would probably require that the retentate from RO be first concentrated using a suitable method. The reaction is typically carried out using solid sodium sulphate and carbon.

$$Na_2SO_4(s) + 2C \rightarrow Na_2S(s) + 2CO_2 \qquad \Delta H = +203.7kJ/mol \qquad (15)$$

The course of the reaction can be divided into four stages, the first of which is the period, during which the melting of the material begins. The second is the main stage, during which reaction according to Equation (15) is dominating and the all of the $NaSO_4$ is melted. The third stage consists of a "settling period", during which the amount of sodium sulphide in the reaction mixture increases, causing it to turn mushy. In this stage carbon monoxide is formed according to Equation (16). The carbon monoxide burns over the molten reaction mixture. At this stage, it is imperative that the melt is left undisturbed. Otherwise, the formation of an oxidized form of the sulphide can take precedence in the process. The fourth and last stage is the one, where remaining sodium sulphate fractions react towards sulphides. The fourth and last stage is the one, where remaining sodium sulphate fractions react towards sulphides. (Roth 1964)

$$Na_2SO_4(s) + 4C \rightarrow Na_2S(s) + 4CO \qquad (16)$$

The behaviour described above can be explained with the phase diagram of the Na_2SO_4 – Na_2S system in Figure 17. The formation of carbon dioxide begins at about 730 °C and after further heating, the reaction mixture turns pasty and after that solid. (Lange, Triebel 2000)

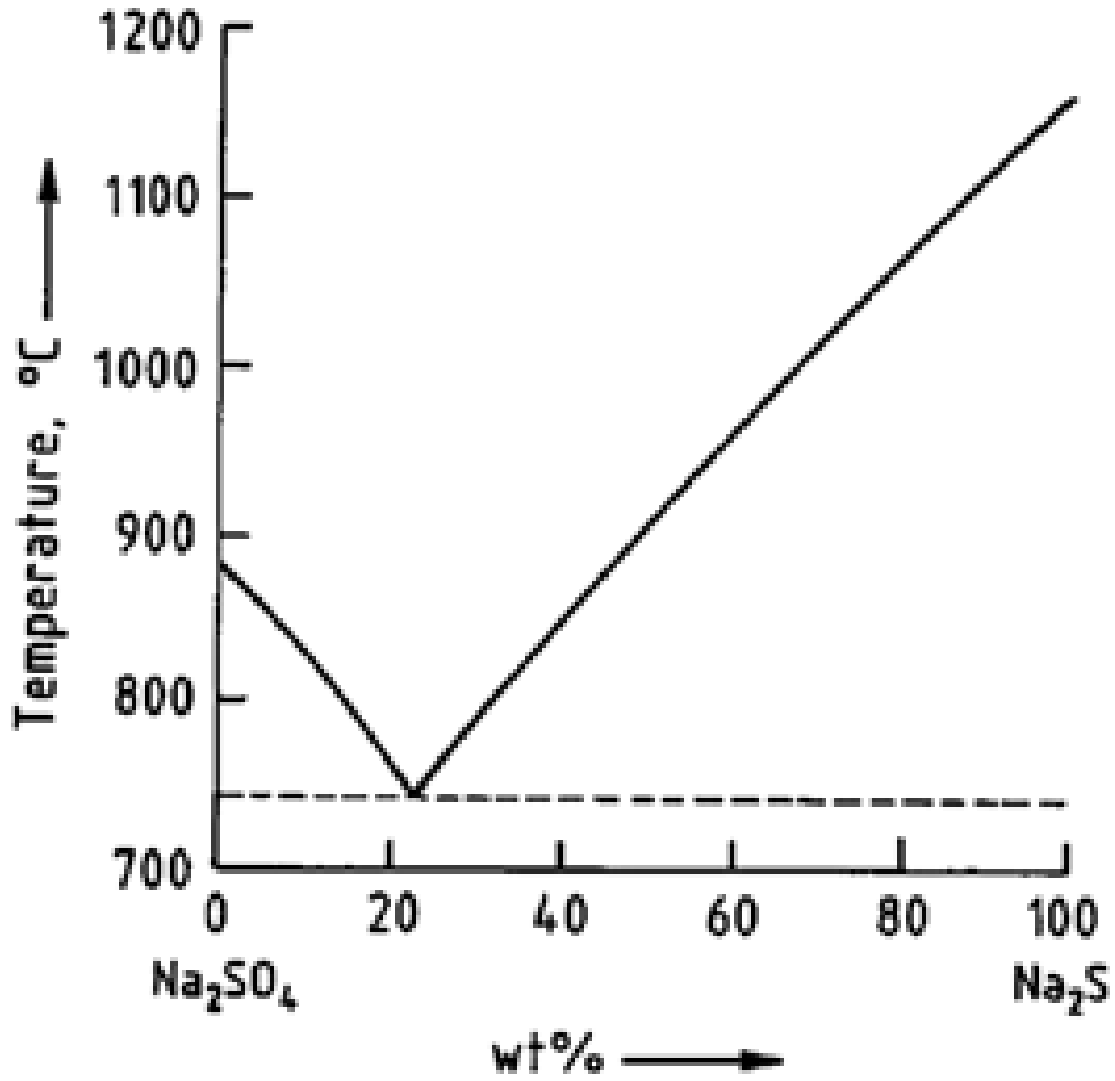

Figure 17. Phase diagram of the Na_2SO_4 – Na_2S system (Lange, Triebel 2000).

The rate of reaction using a solid phase reducing agent is rather modest as long as the reaction mixture is in solid state. As the reaction mixture is melted, the rate of reaction

increases rapidly. With an addition of calcium oxide (CaO), the rate of reaction can be accelerated at temperature beyond the dissociation point of $CaCO_3$, in which carbon dioxide binds itself with CaO. The temperature required for the beginning of the reaction depends on the quality, density, and purity of the carbon used, but is usually between 750 – 880 °C. The eutectic point of the reaction mixture containing 30 – 40 % Na_2S is typically a bit over 700 °C. More bituminous carbon leads to a lower temperature needed for the reduction reaction. Figure 18 depicts (Roth 1964)

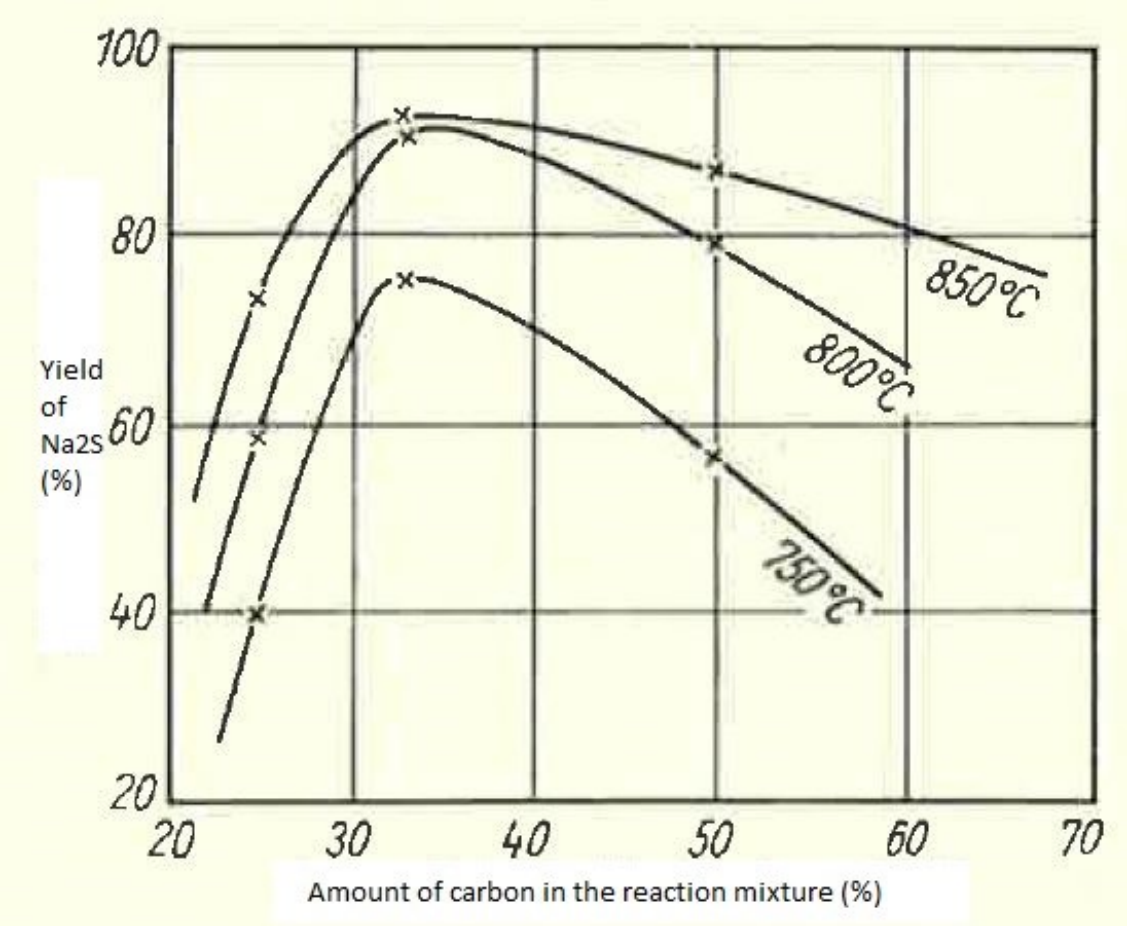

Figure 18. Na_2S yield as a function of the amount of carbon in the reaction mixture in different temperatures (Roth 1964).

Roth (1964) proposes the following procedures for the planning of the reduction process. First, the consumption of carbon during briquetting of the raw material mixture should be

reduced. Also, after 20 minutes of warming, and with a mixture of 83.4 m-% of $NaSO_4$ and 16.6 m-% of charcoal, corresponding roughly to mole ratio 1:2, the reaction at 850 °C is in an effective state. (Roth 1964) The reduction of sodium sulphate into sodium sulphide can be carried out also with gaseous reducing agents, such as H_2, CO, or mixture of hydrocarbons. (Tiwari 1993)

Similar technology for the reduction of barium sulphate to barium sulphide has been tested in pilot scale for a mine water application in South Africa. The idea is an alkali – barium – calcium (ABC) desalination process that could potentially represent an example of a zero waste technology. The process is essentially an integrated lime/limestone neutralisation process, which is combined with sulphate removal carried out with barium carbonate ($BaCO_3$) and also a sludge processing step. With the use of dewatering and thermal processes, barium sulphide (BaS) and calcium oxide (CaO) can be recovered from the sludge produced in the desalination stage of the process seen in Figure 19. (Mulopo, Motaung 2013)

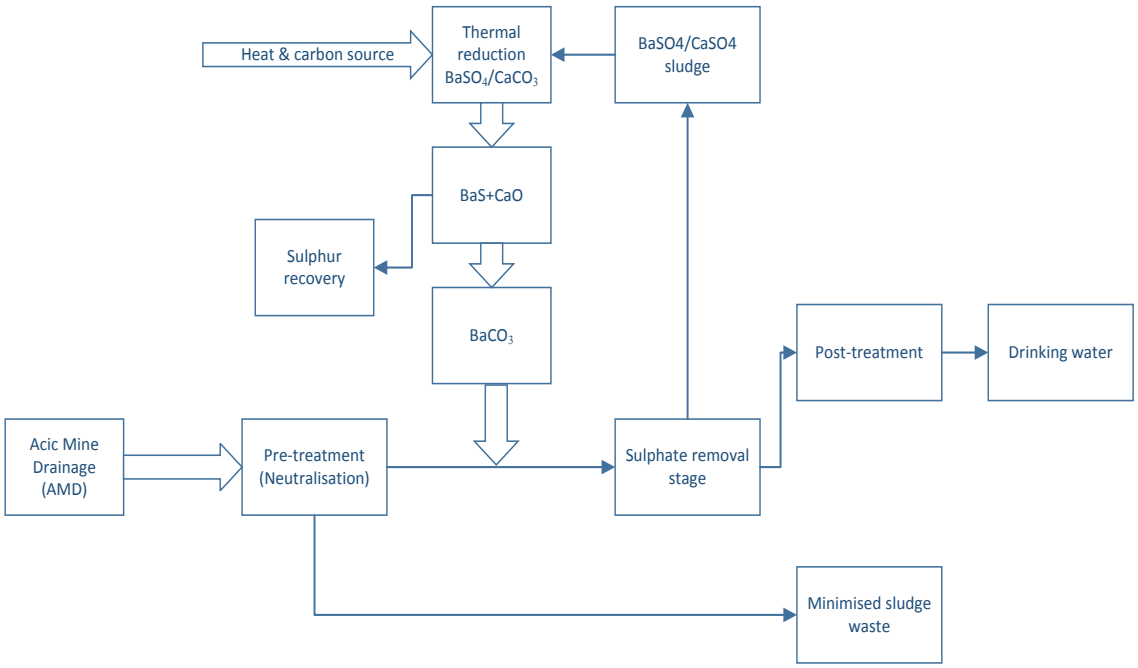

Figure 19. The ABC chemical desalination technology principle (Mulopo, Motaung 2013).

5.6 Eutectic freeze crystallisation

The idea of freezing a solution for the separation of water and solutes, Eutectic freeze crystallisation (EFC) can be considered an extension of the freeze crystallisation process. It utilises the density differences of the salt and water produced in order to generate effective separation. As can be deduced, EFC process is operated at the eutectic point, which is where both ice and salt crystallize. Hence, the problematic mixed salt product formation can be avoided through the production of multiple pure salts, which are formed at their characteristic crystallisation temperatures. This technology has been tested on multi-component, hypersaline brines from the eMalahleni Water Reclamation Plant (EWRP) in South Africa. (Randall et al. 2011)

Figure 20 describes the principle of EFC process. It depicts a basic phase diagram of a binary aqueous solution. Point 1 describes a typical starting point for a wastewater stream, which usually contains a quite low concentration of dissolved solids. Thus, ice usually crystallises first, due to the dilute nature of the solution. Therefore, the starting point (1) is to the left from the eutectic point, a region where ice is the first to crystallise. Point (2) is reached, when the unsaturated solution is cooled until the first crystal of compound A forms. Upon further cooling, the eutectic point is reached and both compounds A and B crystallise. If the concentration of the solution is higher than the eutectic concentration, the salt will crystallise first with the ice crystallising at the eutectic point. (Randall et al. 2011)

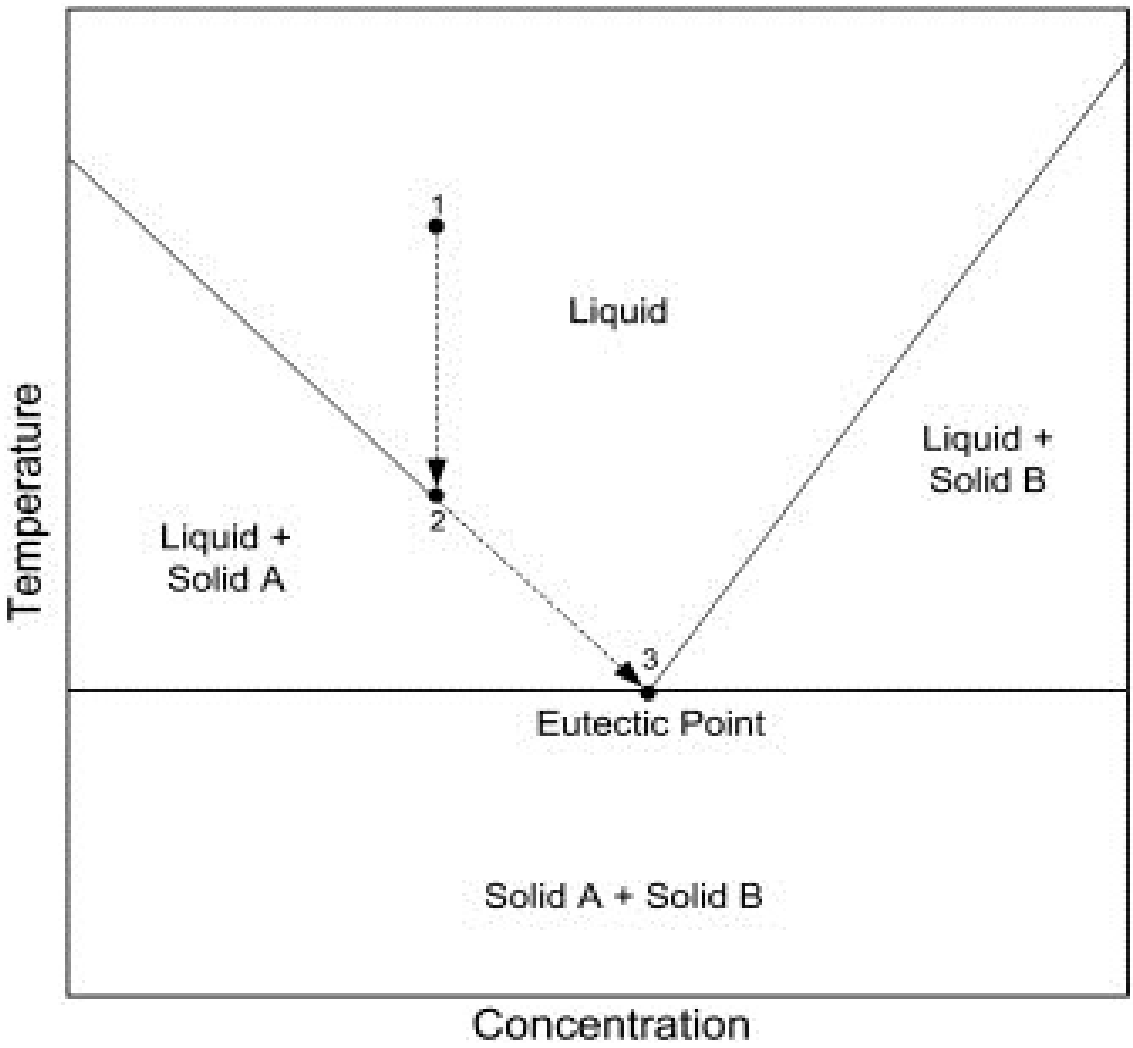

Figure 20. Binary phase diagram showing the eutectic point (Randall et al. 2011).

What makes the EFC such a promising technology for the treatment of RO retentates, is the considerable savings in energy usage it enables. This is because the heat of fusion of ice (6.01 kJ/mol) is much lower than water's heat of vaporisation (40.65 kJ/mol). (Pérez-González et al. 2012) The precedent case in South Africa with handling of a similar retentate than in this case offers an interesting opportunity to examine how to apply this method in this case. Another benefit of using this technology is that pure sodium sulphate is precipitated, which can be utilized. Most important applications for sodium sulphate come from cellulose-fibre industry and from the manufacture of glass and detergents. In addition to these, sodium sulphate is also used in dyeing technology, electrochemical

metal treatment, animal feeds, heat accumulators and sponge manufacturing, among others. (von Plessen 2000)

APPLIED PART

6 Analysis of the literature part

6.1 Comparison of the technology options

The technology options for the treatment of the retentate from the RO plant have been examined and compared in APPENDIX 1. The methods that stand out from the comparison as possessing the most potential in the treatment of the retentate include forward osmosis, electrodialysis, bioreactor, carbothermic reduction, eutectic freeze crystallisation, and as a safer option chemical precipitation. These methods are expected to provide a way to not only reduce the amount of sulphate in the retentate but also to offer recycling possibilities, which would make the process more feasible. The methods left out of the examination at this point are omitted because economics or maturity of the technology is found lacking. The choice of the most promising options depends on the suitability of the methods for treatment of the retentate in this study. There are also other projects ongoing on this subject, and eutectic freeze crystallisation, forward osmosis, and bioreactor either have been or are being examined in this context. Therefore, these methods are left out of the scope of this study. Also, electrodialysis is deemed too complicated a method to examine in this study, and therefore it is also left out of this study.

6.2 Methods chosen for further examination

In the applied part of the study, two different process concepts are constructed and examined. One of these concepts is based on thermal processes and the other relies on chemical precipitation. Due to the nature of the thermal process, it is studied using simulation models without experimental examination. The method modelled in this study using simulation is the carbothermic reduction preceded by the further concentration of the retentate and the following crystallisation of sodium sulphate. This method is

examined using two different scenarios with different feed streams. The concentration and crystallisation of the retentate is of interest in itself, and therefore they are also examined with some attention. Evaporation and evaporative crystallisation are considered mature technologies and used in the treatment of different types of waters with high salinity. The reduction of sodium sulphate using carbon is also a well-known concept and used widely in the pulp and paper industry. In addition to using graphite, the reduction of sodium sulphate to sodium sulphide has also been carried out using H_2, CO, or gaseous hydrocarbons (Littlewood 1961). There are, however, no precedents found in literature about the utilisation of the carbothermal reduction of Na_2SO_4 in the treatment of RO retentate or mine waters. The waters treated from pulp and paper industry differ greatly from the waters from mining industry. The retentate to be treated lacks the organic carbon source that the water from pulp and paper industry contains, which leads to a need for outside carbon source.

Based on the idea of Mulopo & Motaung (2013) a process principle for the treatment of the RO retentate stream is presented in Figure 21. The retentate from the RO lines is first treated to remove the gypsum. This can be done using thermal methods. After gypsum removal, the retentate is concentrated further by evaporation concentration, which is followed by a crystallisation stage. The sodium sulphate is not dried completely; some water is left to enable pumping of the sodium sulphate slurry. The slurry is led to a reactor, where the Na_2SO_4 is reduced carbothermally using graphite. Graphite is chosen as the carbon source in this case because it is readily available in the mine site. The formed Na_2S is separated from the gases formed (H_2O, CO, CO_2) and is led back to the metal recovery stage of the process.

Because of the nature of the process and the considerable water content in the retentate stream, this method is expected to have substantial energy demand. Therefore, the energy economy of the process is the largest challenge to overcome in order to successfully utilise this method. This process principle is approach through simulation because to test it in practise would not be possible during this project.

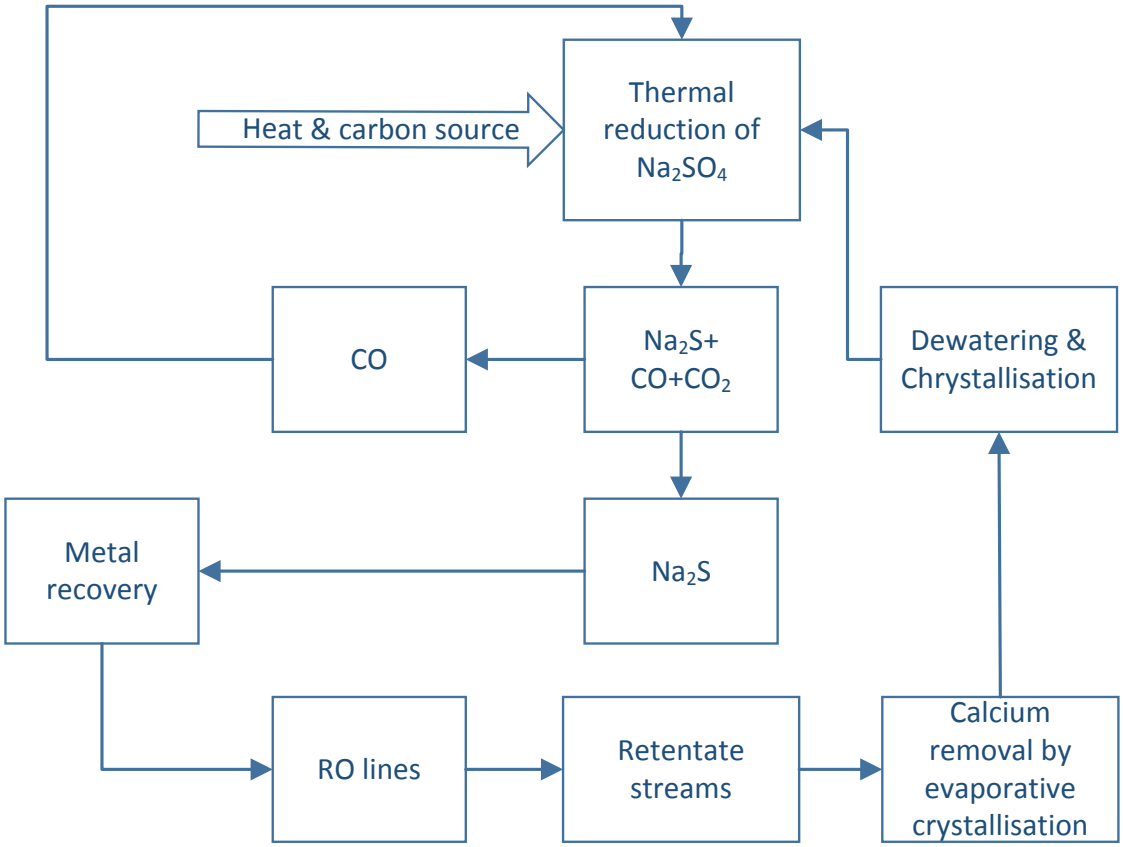

Figure 21. The proposed first process principle.

In addition to the previously presented thermal treatment method, the precipitation of sulphate as gypsum using hydrated lime is considered as an alternative option. The goal is to reduce the amount of sulphate in the retentate through gypsum formation and at the same time concentrate lye (NaOH) in the solution (Equation 17). Sodium hydroxide could thereafter be collected and recycled back into the process to be used in the same manner as hydrogen sulphide in the sulphide precipitation of metals. However, the equilibrium reached by the constituents in the solution in increasingly alkaline conditions can become problematic for this method. (Schoeffel, Barton 1956). Precipitation as gypsum is usually used as a neutralising method with the precipitate formed as a by-product. Most of the applications and studies on this method are on acidic or neutral feed streams. The situation in this study differs fundamentally, because the retentate is already alkaline and the

precipitation is the main goal. Therefore, attention needs to be paid to the effect of rise in pH level to the dissolution of slaked lime and the precipitation of gypsum. This possibly problematic effect of rising alkalinity could be counteracted by using a pH lowering reagent to neutralise the hydroxide ions released into the solution, which would allow for more $Ca(OH)_2$ to dissolve. To use this method, however, would prevent the further concentration of NaOH into the retentate.

$$Na_2SO_4(aq) + Ca(OH)_2(aq) + 2H_2O\ (l) \rightarrow CaSO_4 \cdot 2H_2O(s) + 2NaOH(aq) \qquad (17)$$

The principle for the second process concept contains the addition of $Ca(OH)_2$ to the retentate and mixing the reaction solution to precipitate as much gypsum as possible. At the same time, the concentration of NaOH in the solution increases and if high enough concentration can be reached, NaOH could be recycled back into the process. Alternatively, if the addition of neutralising reagent is required, the solution with considerably lower sulphate content can be utilised. Simple process principle can be seen in Figure 22. The second process principle is examined by carrying out a series of laboratory test to determine how the presented system actually functions. Especially interesting is to determine how large an effect the rise in alkalinity has on the dissolution of $Ca(OH)_2$ and the precipitation of gypsum.

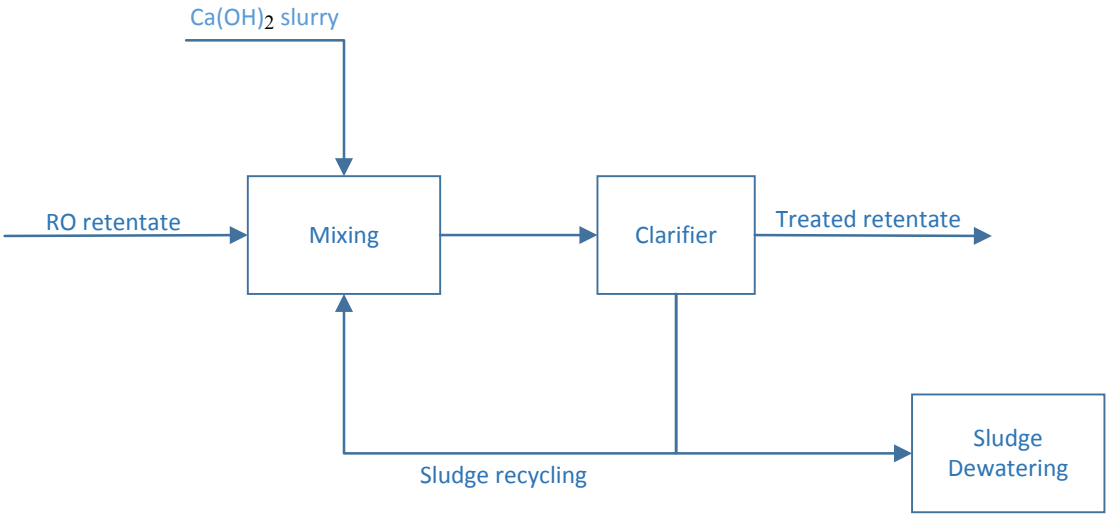

Figure 22. The proposed second process principle.

The application of the presented process requires the acquisition of equipment for the addition of the $Ca(OH)_2$ to the retentate. This requires a storage tank, conveyer, mixer, and mixing tank, where the precipitation occurs. Lime precipitation is already in use at the mine site, which suggests that at least some of the equipment required is already in place. During the precipitation process, considerable amount of sludge is formed, which requires handling. After precipitation the solution is led to a clarifier, after which the sludge goes to dewatering process. In bulk applications, gypsum sludge is often dried using a horizontal vacuum belt filter (Figure 23).

Horizontal vacuum belt filter uses a continuously moving horizontal belt of filter medium, which moves between two rollers. The cake, which is formed in the feed zone, goes through dewatering, washing, and drying stages, after which it is discharged when the belt turs around the other roller. (Sutherland , pp. 134)

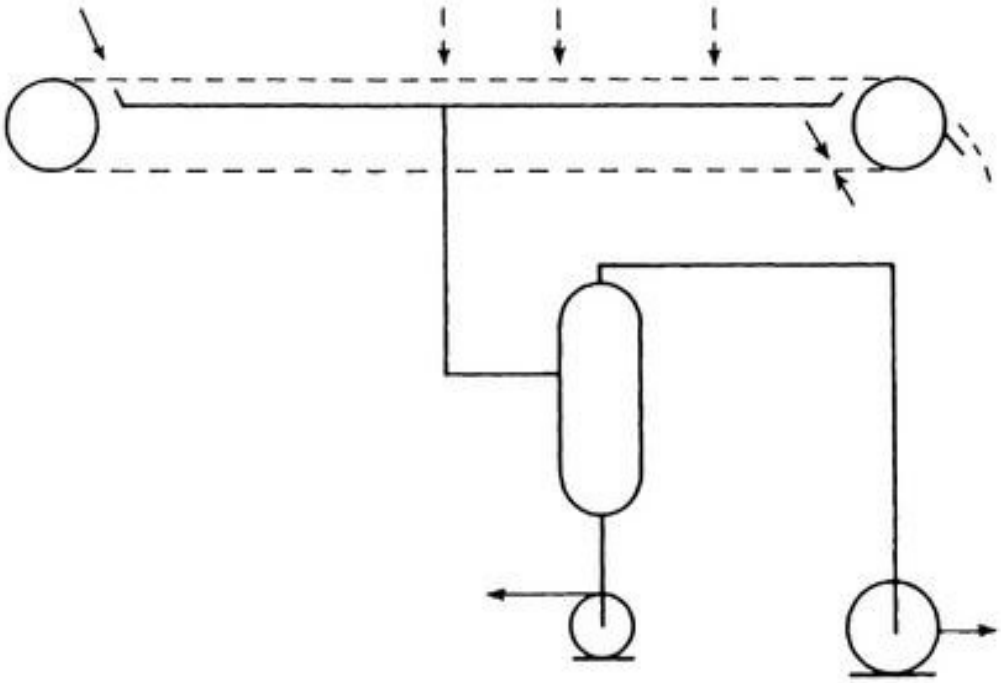

Figure 23. A schematic of a horizontal vacuum belt filter. (Svarovsky 2013, pp. 466)

7 Case study

7.1 Water balance of the process

Figure 24 depicts the water balance of the process. It should be noted that the values presented here are not constant but vary constantly. The situation presented here is momentary. PLS is led from the primary heaps to metal recovery, where CuS, ZnS, and mixed NiS and CoS products are recovered. Subsequently, iron is precipitated together with aluminium as sulphides. After iron precipitation is the final neutralisation stage, after which the alkaline overflow from the second concentrator is led to the raw water pond 2 (RW2). The stream is led through the RW2 pond to the RO plant. The stream has its own pipelines, and therefore it does not come into contact with the water in the pond, which contains water from different sources making it extremely scaling.

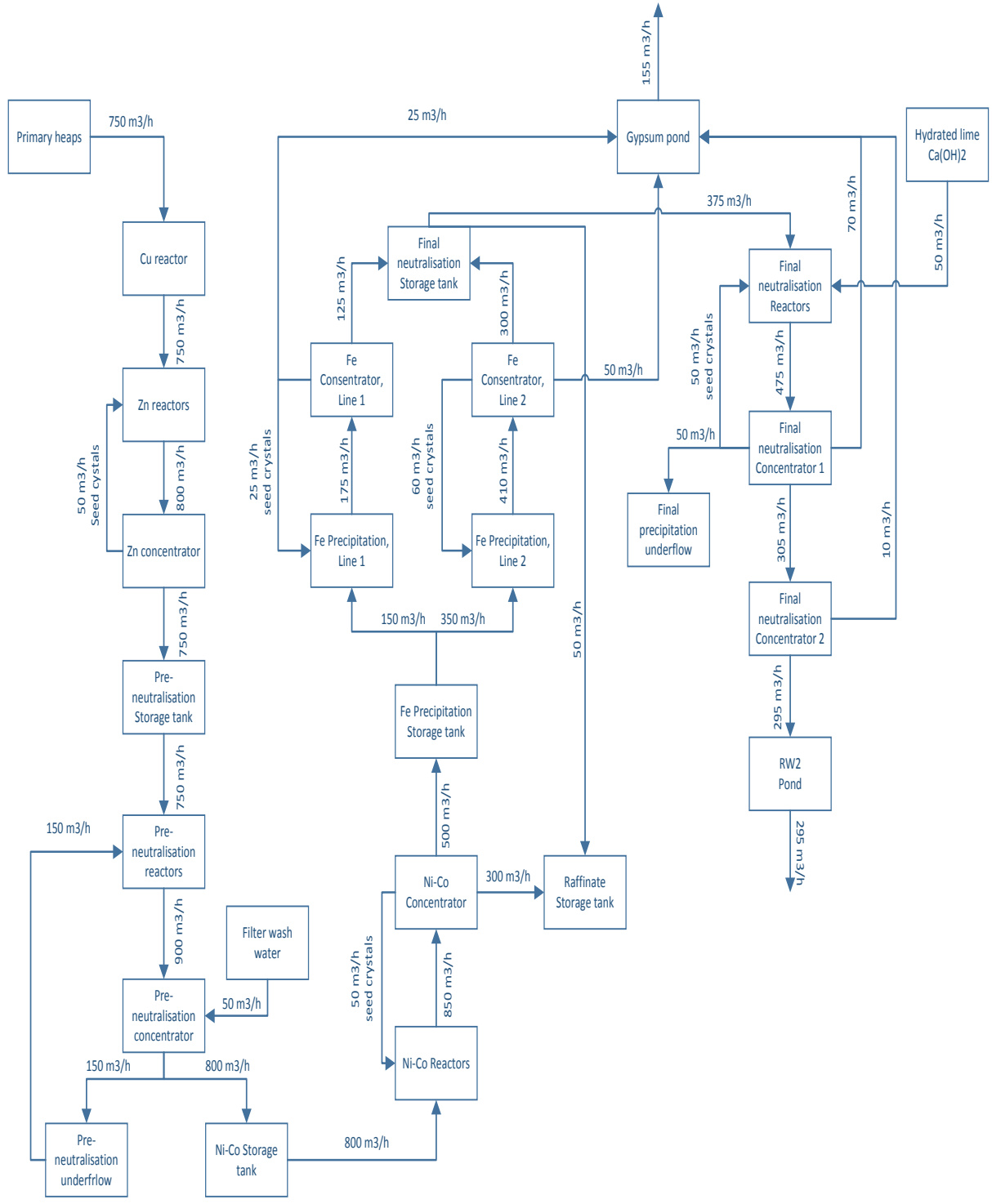

Figure 24. Water balance of the process.

7.2 The RO plant

Figure 25 shows the water balance for the RO plant. Typically, two out of the three existing RO lines are running at the same time. Each line has the maximum capacity of 150 m^3/h and therefore, total flow to the RO plant is 300 m^3/h maximum. Due to the limited capacity of the pre-filtration system, only enough water for one line can be taken from the pipelines of the overflow of the final neutralisation. The rest of the water needed is taken directly from the RW2 and it bypasses the first sand filters, which are the bottleneck in the pre-treatment system. This causes increased fouling of the pressure sand filters as the water from RW2 pond includes significant amounts of slurries.

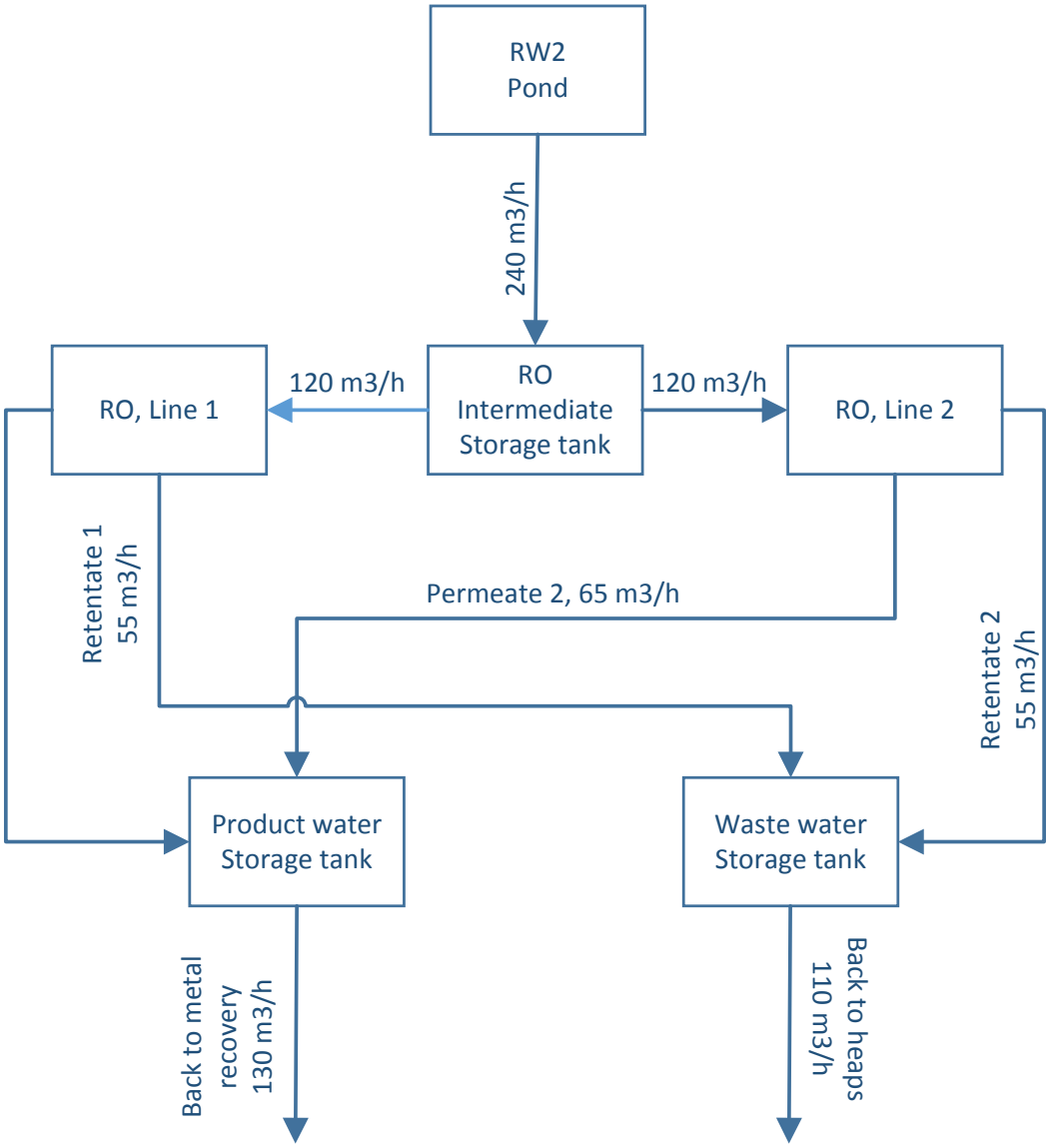

Figure 25. Average water balance of the RO plant (with two lines running)

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7.3 The retentate stream

The basis for the simulations and laboratory studies is the retentate stream from the RO plant. Table 8 depicts the average composition of the retentate, during a period of a week. As can be seen, the retentate stream contains mostly dissolved sodium sulphate (Na_2SO_4) and calcium sulphate ($Ca(OH)_2$). The concentrations of other species are relatively low.

The pH of the retentate is kept close to 10. This is done to prevent scaling in the RO system.

Table 8. Average composition of the RO retentate.

Species	**Concentration (mg/l)**
Al^{3+}	<0.154
Ca^{2+}	936.3
Co	<0.033
Cu	<0.066
Fe	<0.066
K^{+}	27.2
Mg^{2+}	90.8
Mn^{2+}	0.04
Na^{+}	3640
Ni	<0.022
Si	0.417
Zn	<0.033
SO_4^{2-}	10600

7.4 The antiscalant

Antiscalants, which are synthetic chemicals, are used in RO processes to inhibit precipitation and following membrane fouling. These compounds are added to the RO feed stream. The working principle is that antiscalants are adsorbed onto growth sites as crystals nucleate thus preventing further growth and precipitation. Another way for antiscalants to prevent precipitation is through particle dispersion. (Greenlee et al. 2010) Antiscalants are vital in the operation of an RO plant, but they can cause problems with the treatment of the formed retentate. Therefore, it is important to determine the effect of the antiscalant on the treatment of the RO retentate. The presence of antiscalant in the retentate, in part, explains the higher amount of dissolved $CaSO_4$ in the stream than could otherwise be expected.

The antiscalant used in the Terrafame mine contains a potassium salt of a phosphonic acid, the structural formula of which can be seen in Figure 26. This antiscalant is recommended especially for calcium sulphate control. (Greenlee et al. 2011) Therefore, it is to be expected that the presence of antiscalant will somehow effect the precipitation process.

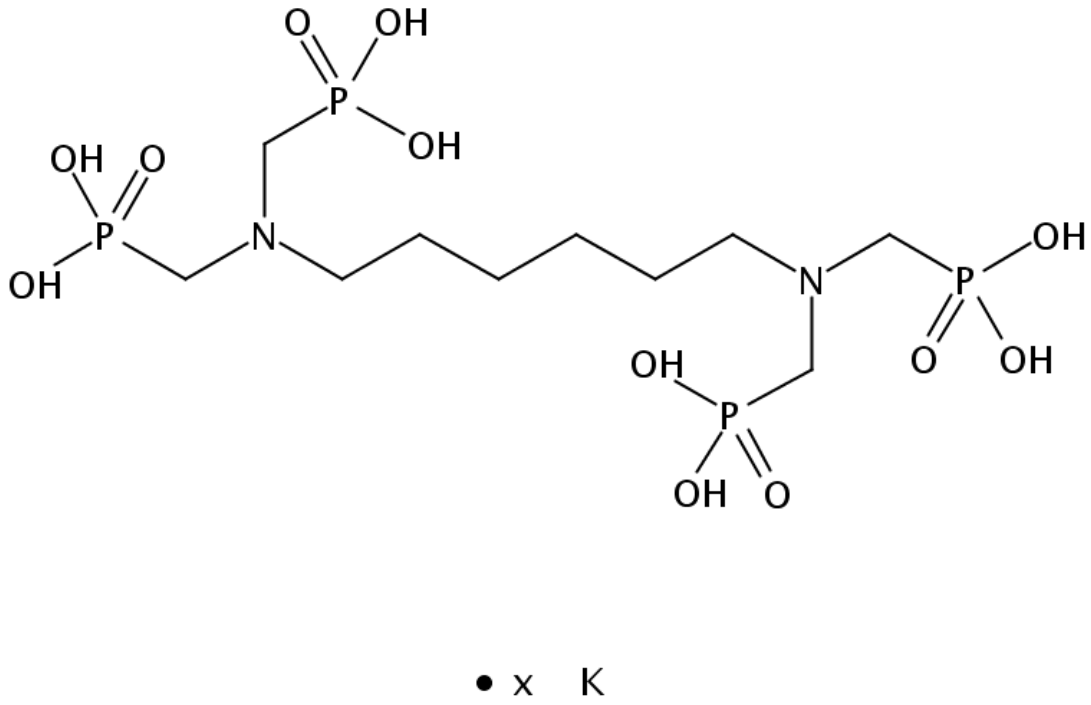

Figure 26. Chemical formula of the antiscalant used in the process.

8 Methodology

The methods used in the applied part of the study are simulation for the first process concept and laboratory experiments for the second process concept. For both of the concepts, the main operating costs are evaluated.

8.1 Simulations

The further examination of the reduction of sodium sulphate to sodium sulphide is carried out using Aspen Plus simulation program. The process model constructed is based on earlier conducted studies and patents on similar processes (Schoeffel, Barton 1956, Feldbaumer et al. 1980, Wilhelm 1970, White, White 1936).

Based on these and other sources the reaction between carbon and sodium sulphate begins in solid state and continues in liquid state, during which the rate of reaction also speeds up. Based on previously listed literature, the reaction conditions of 1 bar and 950 °C are chosen. The higher temperature is chosen due to the usage of graphite in the reactor. Graphite has been found to require higher temperatures than other solid carbon sources to effectively reduce Na_2SO_4 to Na_2S (White, White 1936). The Aspen simulation is constructed using the electrolyte model and the base method ELECNRTL, which is an electrolyte NRTL model with Redlich – Kwong equation of state meant for aqueous and mixed solvent applications. Components present in the simulation are generated with the electrolyte wizard tool. All salt reactions and crystallisation are generated using the chemistry defined by the electrolyte wizard.

The simulations are carried out based on two different scenarios. In the first, the original retentate, which still contains calcium sulphate, is used as the feed stream. The second scenario is one, in which the calcium sulphate has already been removed from the retentate along with half of the water volume.

8.1.1 Specifications

The feed stream in the simulation is modelled after the retentate stream from the RO plant, with some simplifications. The rather low metal concentrations are left out of the feed solution in order to make the model simpler. Also, in the second scenario of the simulations the calcium sulphate in the reject is presumed to have been removed by pre-treating. Therefore, there are two feed stream specifications, which can be seen in Table 9 and Table 10.

Table 9. Specifications of the feed stream for the first scenario.

Temperature	25 °C
Pressure	1.6 bar
H_2O	99300 kg/h
Na_2SO_4	1120 kg/h
$CaSO_4$	320 kg/h

Table 10. Specifications of the feed stream for the second scenario.

Temperature	25 °C
Pressure	1.6 bar
H_2O	49650 kg/h
Na_2SO_4	1120 kg/h

8.1.2 Simulation units

Most of the water is evaporated and anhydrous Na_2SO_4 is crystallised before leading the stream to the reactor to be reduced thermally with graphite to Na_2S. The overviews of the simulated processes are depicted in Figure 27 and Figure 28. The stream ID's correspond

with the stream ID's in the stream tables in APPENDIX II and APPENDIX III. A more detailed description of the different process units follows.

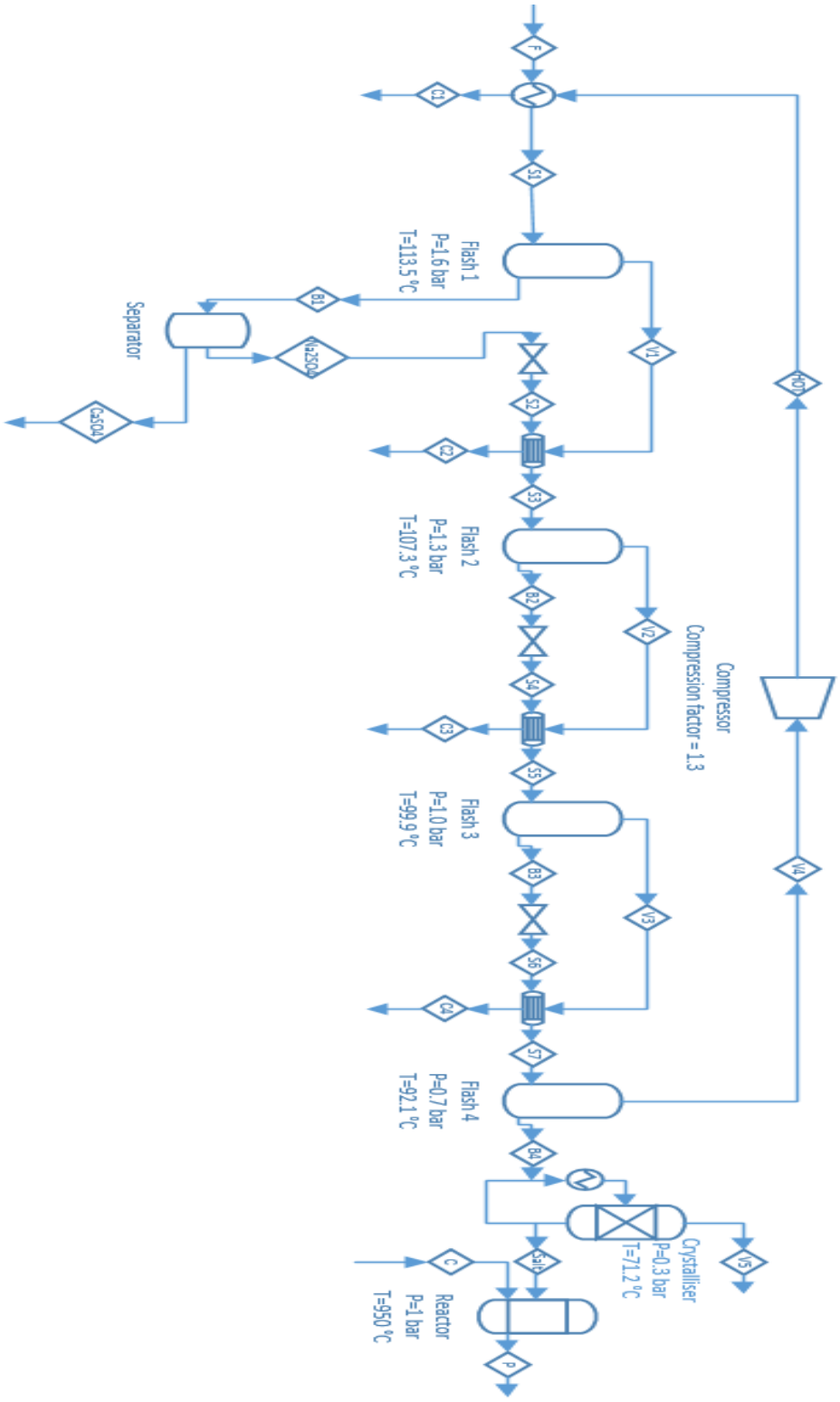

Figure 27. Schematic of the simulated process, scenario 1.

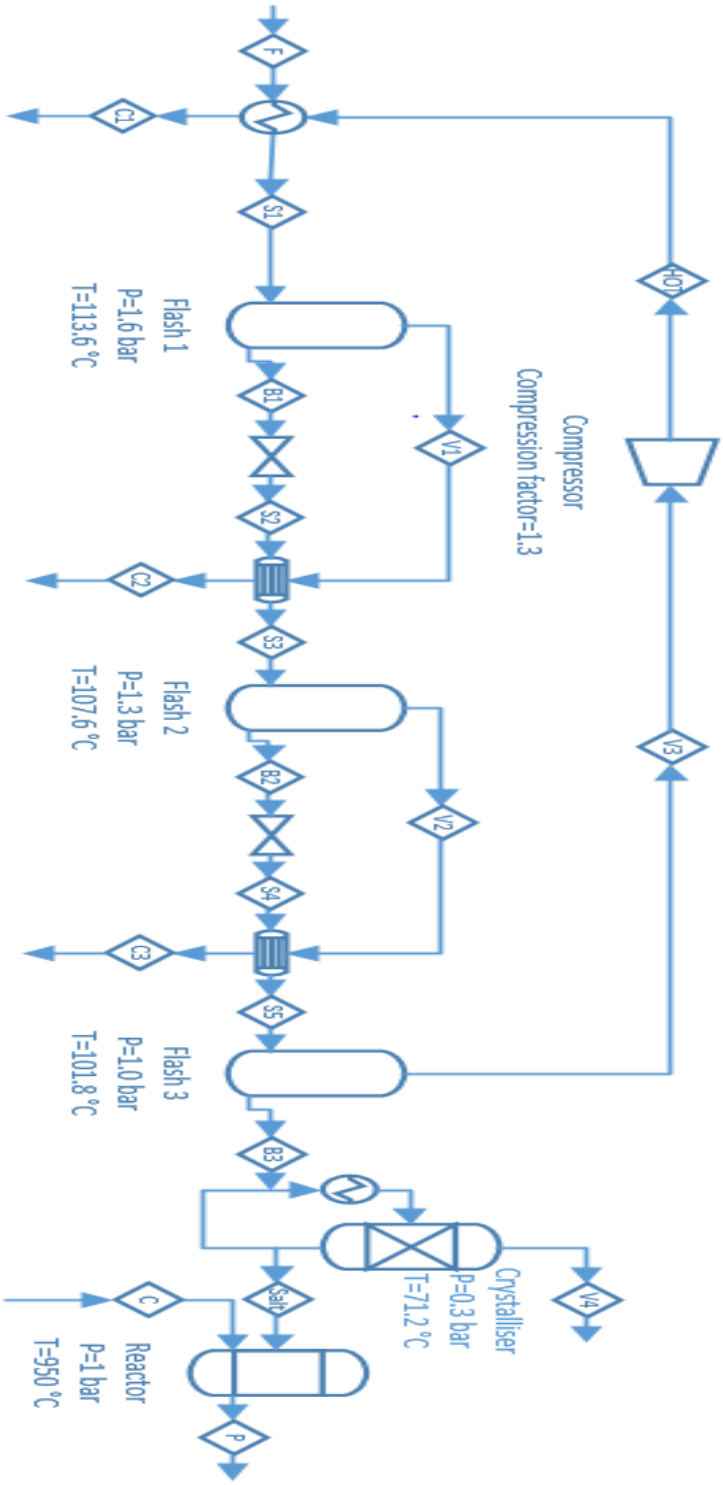

Figure 28. Schematic of the simulated process, scenario 2.

Evaporation

The evaporation is modelled based on a multi-effect evaporation mechanical vapour compression (MEE-MVC) process (Nafey et al. 2008). The vapour produced in each stage is used to evaporate water in the next stage. The evaporators after the first one are modelled as consecutive adiabatic flash tanks, with valves as pressure changers and counter current heat exchangers that use the condensing vapour from the previous flash tank to heat the stream entering the next flash tank. The pressure drop between flash tanks is 0.3 bars. With evaporation the retentate is concentrated to near saturation concentration. From Figure 3 can be seen that the solubility of sodium sulphate in water is around 28 – 30 wt. % in the temperature range of 80 – 100 °C. After the evaporation stages, the nearly saturated solution is led to a crystalliser. The concentration of the solution going to the crystallisation stage is circa 25 wt. %.

Separator

The calcium sulphate crystallised in the first evaporation stage is separated from the sodium sulphate containing solution. The model used is a component separator, which separates the components based on specified flows or split fractions.

Crystalliser

The solution from the evaporation stages is led to the evaporative crystalliser, where the pressure is dropped to 0.3 bar and where most of the remaining water is removed. The temperature of the crystalliser is 71.2 °C. The crystallising salt is anhydrous sodium sulphate Na_2SO_4. The specifications for the crystalliser are the operating pressure 0.3 bar and the vapour outlet stream 2400 kg/h. The recirculating fraction is 0.2. The retentate is not dried completely so that the crystallising solution can be recirculated and that the product stream can be pumped easier to the reactor.

Compressor

An isentropic compressor is used to compress the vapour from the last flash stage. The compressed vapour is used to heat the feed to the first evaporation stage. The pressure ratio of the compressor is 1.3 and both isentropic and mechanical efficiencies are set at 0.7.

Reactor

The reactor model used in the simulation is a Gibbs reactor, which is a rigorous reaction and multiphase equilibrium model based on Gibbs free energy minimisation. This model was chosen due to the lack of kinetic data on the reduction reaction found in literature. The specifications for the reactor were the temperature of 950 °C and pressure of 1 bar. The crystallised salt and the remaining water are led to the reactor with pulverised graphite. The amount of graphite used is based on data provided by Roth (1964), from which the amount of carbon is 40 % of the amount of mixture containing Na_2SO_4 and carbon. Therefore, the amount of graphite used is 740 kg/h.

8.2 Laboratory testing of precipitation with $Ca(OH)_2$

8.2.1 Background

The second process concept, relying on gypsum precipitation with hydrated lime ($Ca(OH)_2$) for the treatment of the retentate stream is tested in the laboratory scale. This is a much used method, which is also considered as the best available method for mine water treatment. (Anonymous2009). However, there have been few occasions that this method has been used to treat alkaline solutions like the one examined in this study. The results from previous laboratory and pilot scale testing, conducted by Davies et al. (2012) indicate that with the use of this method, the sulphate content in the retentate could be lowered to significantly below 5000 mg/l.

Calcium sulphate is a compound that can be encountered in three different forms: gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite, and hemihydrate ($CaSO_4 \cdot 0.5H_2O$). In most of the water treatment applications, the predominant phase is gypsum. (Davis et al. 2012) The solubility of different forms can be seen in Figure 29. Based on it, it is to be expected that the precipitated $Ca(OH)_2$ is in the form of gypsum, as long as ambient temperature is used.

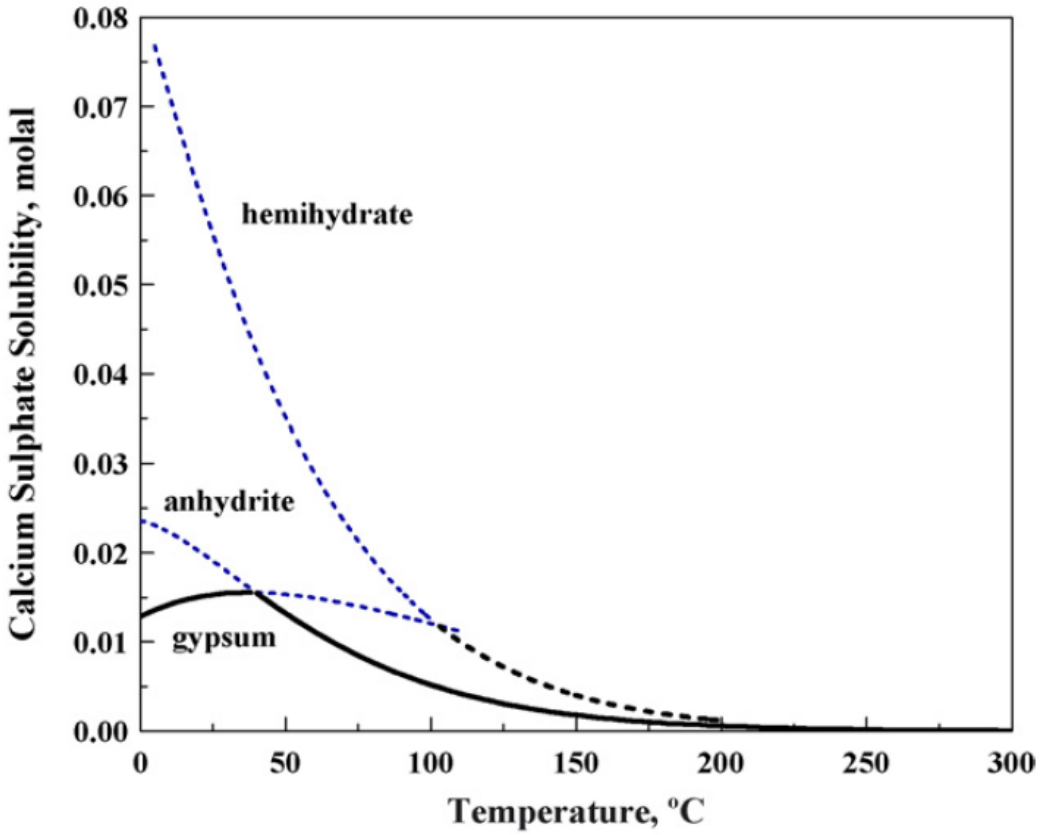

Figure 29. The solubility diagram for different forms of $CaSO_4$ (Azimi et al. 2007)

Equations 18 – 20 represent the common dissociation equilibria for the system studied in these experiments (Yuan et al. 2010). These equilibria determine how much of the sulphate in the retentate can be removed using this method.

$$CaSO_4 \cdot 2H_2O(s) \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \quad (18)$$

$$Ca(OH)_2(s) \leftrightarrow Ca(OH)^+ + OH^- \quad (19)$$

$$Ca(OH)^{+} \leftrightarrow Ca^{2+} + OH^{-} \quad (20)$$

Yuan et al. (2010) have studied the solubilities of both slaked lime and gypsum in temperatures ranging from 25 to 75 °C. Results from these experiments can be seen in Figure 30 and Figure 31. From them it can be clearly seen that the solubility of slaked lime decreases as pH increases, which can be explained with common ion effect. Contrary to the behaviour of slaked lime, the solubility of gypsum seems to increase as the pH increases up to a point, and after the maximum, it starts to come down again. A viable explanation for the increase in the solubility is the association of Ca^{2+} and OH^{-} ions and the formation of $Ca(OH)^{+}$ ion. The observed decreases in the solubility of gypsum have been suspected to be related to changes in the activity coefficients of calcium, hydroxide, and hydroxyl calcium ions in conjunction with activity of water. (Yuan et al. 2010) It is also worth noting that the solubility of gypsum seems to vary more with increasing temperature in NaOH concentrations above 0.03.

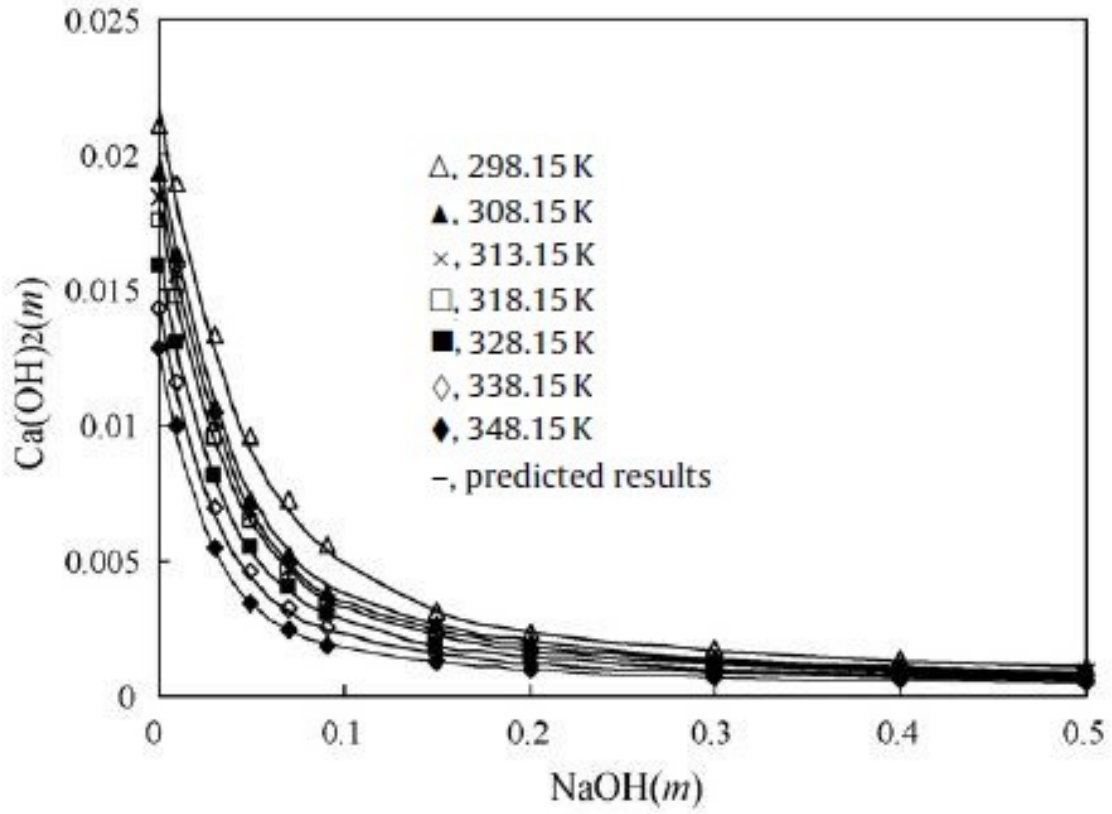

Figure 30. The experimental and predicted solubility of slaked lime in NaOH solutions at different temperatures. (Yuan et al. 2010)

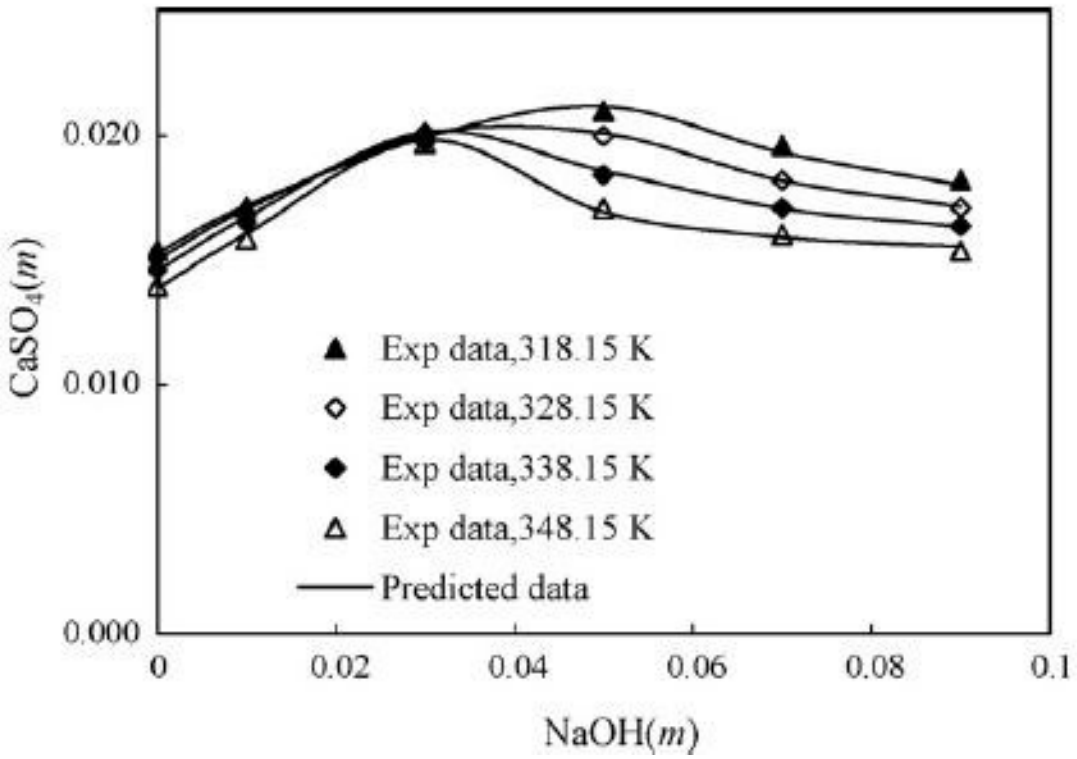

Figure 31. The experimental and predicted solubility of gypsum in NaOH solutions at different temperatures. (Yuan et al. 2010)

The precipitation reaction of gypsum is slightly endothermic (Equation 21), whereas the dissolution reaction of $Ca(OH)_2$ is exothermic (Equation 22). Heats of reaction were determined with HSC Chemistry software.

$$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l) \rightarrow CaSO_4 \cdot 2H_2O \qquad \Delta H_r = 1.72\ kJ/mol \qquad (21)$$

$$Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2OH^-(aq) \qquad \Delta H_r = -17.23\ kJ/mol \qquad (22)$$

8.2.2 Material

The samples used in the experiments are from the 10 litre sample gathered from the RO retentate stream in the Terrafame mine in Sotkamo. An analysis of the sample can be seen in Table 11. The analysis of the sample is carried out a month after the gathering of the sample, due to a malfunction during the original analysis. Therefore, the pH level is

considerably lower than originally measured level of 8.8. However, it should be noted that when measured in the laboratory at Aalto University, the pH level was 7.3.

Table 11. Analysis of the composition of the retentate sample.

Species	**Concentration (mg/l)**
Al^{3+}	0.02
As	<0.0003
Ca^{2+}	916
Cd	<0.0001
Co	<0.001
Cu	<0.002
Fe	0.44
Mg^{2+}	39.5
Mn^{2+}	0.21
Na^{+}	3721
Ni	0.006
Zn	<0.01
U	0.003
SO_4^{2-}	9900
pH	**6.63**

The precipitation reagent studied here is calcium hydroxide ($Ca(OH)_2$), also called hydrated lime or slaked lime. $Ca(OH)_2$ is added to the reaction solution as a slurry (10 wt. %). The slurry is prepared in the laboratory from anhydrous calcium hydroxide by mixing it with water in the previously stated ratio.

In order to lower the pH of the retentate and to enable the continuation of the dissolution of $Ca(OH)_2$ an addition of acid is needed. A suitable reagent is hydrochloric acid (HCl) of 32 wt. %. It is chosen because of a previous study found in literature (Davis et al. 2012), where it has been found effective in this application. The aim is that the added hydrochloric acid consumes some of the hydroxide ions in the solution, thus allowing the dissolution of more calcium hydroxide. This enables more gypsum precipitation and

therefore higher sulphate reduction. An alternative to using HCl as the neutralising agent could be, for example, carbon dioxide (CO_2).

8.2.3 Equipment

The equipment list for the experiment can be seen in Table 12. The stirrer is manufactured for this purpose especially in the workshop of Aalto University. The pH meter was VWR pH-100. The calibration was a three-point calibration carried out using three standard solutions, 4.01, 7.00, and 10.01. The pH of each sample was measured after the 1 hour mixing time.

Table 12. Equipment list for the experiments.

Equipment
pH meter (VWR pH-100)
Temperature sensor (a k-type thermocouple)
Water bath (temp contr)
Thermostat
Stirrer (with a stem)
Magnetic stirrer
Reaction vessel (0.4 litre)
Suction bottle
Filter paper

8.2.4 Method

Pre-tests

Pre-tests are carried out mostly in the same manner as precipitation tests. The objective is to validate the test method: make sure that solid phase is formed. Pre-tests are carried out without the lowering of pH, in order to find out how the precipitation progresses with only

slaked lime. The amounts of $Ca(OH)_2$ used in pre-tests are the stoichiometric, 1.5 times the stoichiometric, and double the stoichiometric amounts required for the precipitation of all of the sulphate in the retentate as gypsum.

Immediately after the addition of the slaked lime slurry, the solution turns milky, and shortly, fine white flakes were observed starting to settle on the bottom of the reaction vessel. Due to this it is determined that mixing of the solution during the addition of the slaked lime is necessary to ensure efficient contact. The mixing is carried out using stemmed mixer with the mixing speed of 160 – 170 rpm. The mixing time is 1 hour. During mixing, the temperature of the reaction solution is monitored and the temperature remains within a fluctuation range of 1°C.

Precipitation tests

Test variables

1. The dosage of $Ca(OH)_2$
2. The dosage of HCl
3. The starting sulphate concentration

The dosages of calcium sulphate tested are set the same as with the pre-tests (stoichiometric, 1.5 times the stoichiometric and double the stoichiometric amount), according to the amount of sulphate in the retentate. The dosages of HCl chosen for testing are also calculated based on the sulphate amount in the sample. The amounts used are approximately: $0.7 \cdot n(SO_4), 0.9 \cdot n(SO_4),\ 1.2 \cdot n(SO_4)$. The dosages used are estimated based on Davies et al. (2012).

The third and final test variable in the experiments is the starting sulphate concentration in the reaction solution. In the first set of experiments, the sulphate concentration of the retentate is the starting concentration, and in the second set of experiments, the starting concentration of sulphate is roughly doubled by evaporating half of the water volume using a rotavapor.

Execution of the experiments

The experiments are carried out at Aalto University School of Chemical Technology in the Chemical Engineering department's laboratory. The study carried out by Davis et al. (2012) has been used as a starting point for the design of the experiments. Experiments are carried out as laboratory batch tests to determine the sulphate reduction that is reached using different slaked lime and hydrochloric acid dosages. A standard amount of 200 ml of the RO retentate is placed in a 400 millilitre glass vessel and stirred with a motorised stemmed stirrer. The reaction system can be seen in Figure 32.

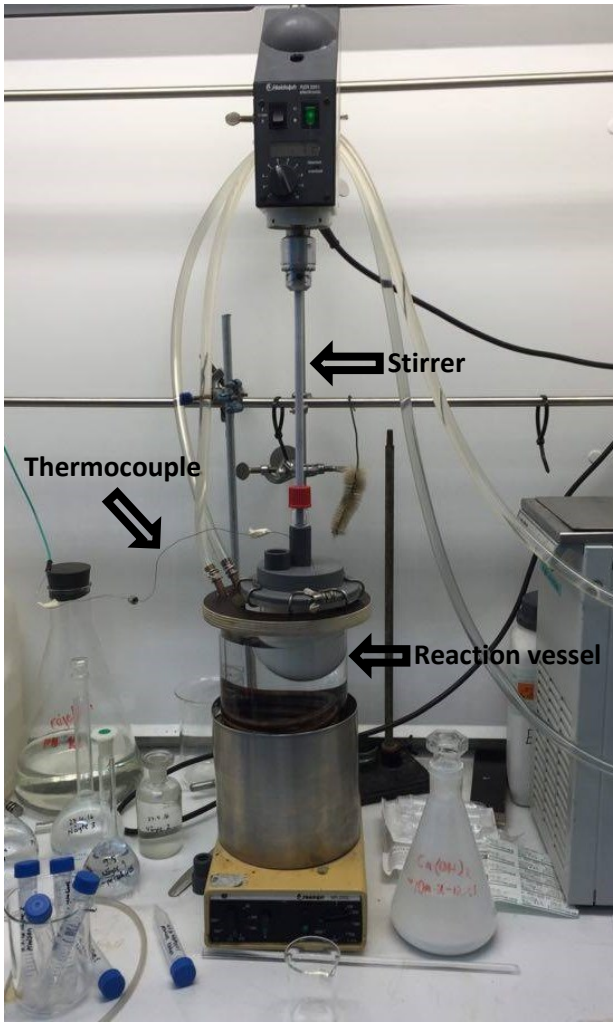

Figure 32. The reaction system.

The HCl is added to the retentate prior to slaked lime with a syringe. The slaked lime slurry is then added to the now acidic solution while stirring the solution lightly, circa 80 rpm. The temperature is kept constant using a temperature controlled water bath, with the thermostat set at 25 °C. All experiments are conducted at atmospheric pressure. After 1-hour residence time the mixing is stopped and the solution is filtered under vacuum using a suction bottle (Figure 33).

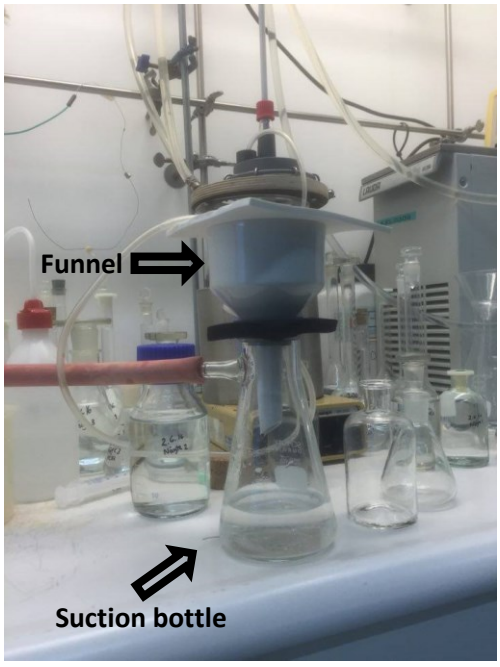

Figure 33. The filtration system.

In order to determine the effect of the starting sulphate concentration on the amount of gypsum precipitation, the second set of precipitation tests are carried out using retentate that has been concentrated using a rotary evaporator. Approximately 45 percent of the water in the original retentate is evaporated. The water bath of the rotavapor is heated to 84 – 86 °C and the vacuum is kept at approximately 0.3 bar level using a diaphragm pump. The system can be seen in Figure 34.

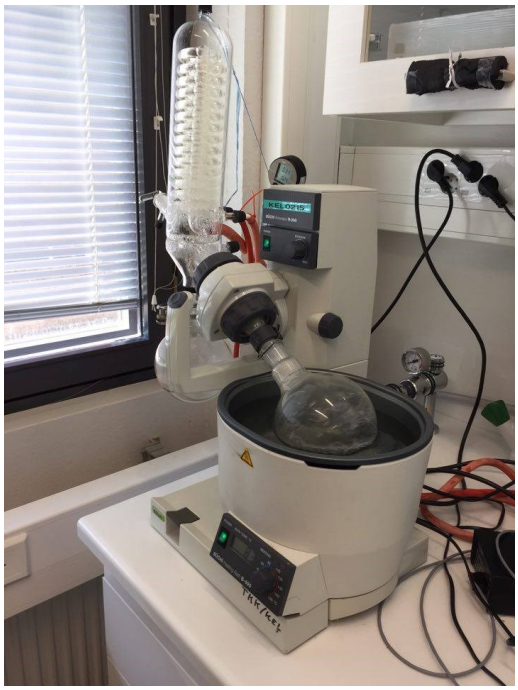

Figure 34. The system for the concentration of the retentate.

The solid phase is washed after filtration with 100 ml of distilled water and the washing liquid is collected. Figure 35 depicts the formed precipitate.

Figure 35. The formed precipitate.

The filtered solution is analysed for the sulphate, sodium, calcium, and chloride concentrations. The sulphate concentration is analysed by measuring the sulphur concentration of the sample and the sulphate concentration is calculated from it. The analyses are outsourced and carried out at the premises of Aalto University School of Chemical Technology. Descriptions of the analysis methods are found in APPENDIX IV.

9 Results and discussion

This chapter presents the key findings of the applied part of this study. This includes the simulation results, mainly the power consumption, and the results from the precipitation tests. In addition, the operating costs of the two examined process concepts are assessed.

9.1 Results of the simulated process

Table 13 and Table 14 present the simulated separation units in the process. Detailed stream tables are found in APPENDIX II and APPENDIX III. The temperatures in the flash tanks start from a bit over 113.4°C, which is a reasonable top brine temperature (TBT), and should prevent serious fouling in the heat exchangers. Another way to prevent fouling is the use of forced circulation evaporators.

Table 13. The simulation units in the first scenario.

Unit	Temperature (°C)	Pressure (bar)	Vapour fraction
Flash 1	113.5	1.6	0.23
Separator	113.5	1.6	-
Flash 2	107.3	1.3	0.31
Flash 3	99.9	1.0	0.46
Flash 4	92.1	0.7	0.86
Crystalliser	71.2	0.3	2400 kg/h (vapour flow rate)
Reactor	950.0	1.0	-

Table 14. The simulation units in the second scenario.

Unit	Temperature (°C)	Pressure (bar)	Vapour fraction
Flash 1	113.6	1.6	0.30
Flash 2	107.6	1.3	0.44
Flash 3	101.8	1.0	0.80
Crystalliser	71.2	0.3	2400 kg/h (vapour flow rate)
Reactor	950.0	1.0	-

9.1.1 Energy consumption

As can be expected, the carbothermic reduction process is quite energy intensive. This is due to the large amount of water in the retentate. This water volume needs to be evaporated and the sodium sulphate crystallised, in order to get the process working as intended. The energy consumption can be greatly reduced with the use of multistage evaporation and subsequent crystallisation. The power requirements of the two scenarios can be seen in Table 15.

Table 15. The power consumptions of the two simulated process scenarios.

Simulation unit	**Scenario 1: Calcium present**		**Scenario 2: Half of the water volume**	
Evaporation	8.665	MW	4.546	MW
Compressor	0.632	MW	0.409	MW
Crystallisation	1.484	MW	1.436	MW
Net power consumption (of concentration and crystallisation)	10.781	MW	6.391	MW
Reactor	4.222	MW	4.373	MW
Net power consumption (of the whole process)	**15.0**	**MW**	**10.8**	**MW**

When looking at the power requirements of the two scenarios, the second scenario seems to require more energy when proportioned to the water volume of the feed. At least part of this is caused by the boiling point rise due to the salts that are dissolved in the stream. The starting concentration of sodium sulphate is double compared to the second scenario. The temperature differences can be seen in the operating temperatures of the flash tanks in Figure 27 and Figure 28. The number of evaporation stages also differs in the scenarios:

in the first there are four and in the second there are three of them. Fewer stages lead to higher energy consumption, but on the other hand, they also induce capital savings.

9.1.2 Operating costs

Most of the operating costs from this process option come from energy consumption and are relatively high due to the thermal nature of the process. Low-pressure steam is used in the first flash tank. Compressor and crystalliser use electricity and the reactor utilises fired heat. The cost of electricity is estimated as being 80 €/MWh (Tilastokeskus 2016). The cost estimates for LP steam and fired heat are taken from Aspen. The costs are calculated so according to the assumption that the plant is operated 8760 hours per year. Table 16 and Table 17 list the utility consumptions and costs for the two scenarios.

Table 16. Utility consumptions of the process (1. scenario).

Utility	**Consumption**	**Price**	**Costs**
LP Steam	14232 kg/h	0.00634 €/kWh	54.8 €/h
Electricity	2116 kW	0.08 €/kWh	169.3 €/h
Fired heat	25332 kg/h	0.0141 €/kWh	59.7 €/h
Total			**2.5 M€/a**

Table 17. Utility consumptions of the process (2. scenario).

Utility	Consumption	Price	Costs
LP Steam	7466.2 kg/h	1.76e-06 €/kJ	28.753 €/h
Electricity	1845 kW	0.08 €/kWh	147.6 €/h
Fired heat	26241 kg/h	3.93e-09 €/J	61.88 €/h
Total			**2.1 M€/a**

The energy costs are substantial and they form most of the operating costs for the process. There are no chemical costs calculated for the process, because the graphite needed for the process is assumed to be available on-site. However, graphite is most probably not found in such a form that would be suitable for utilisation straight away, i.e., some pre-treatment will be necessary.

9.1.3 Value of the product generated

The value of the product produced in the process is estimated in Table 18. The values are calculated with different conversion values because there are varying values for it found in literature. These estimations are based on the amount of Na_2SO_4 on the feed and the fraction of it that is converted into Na_2S. It is assumed that the annual operating hours are 8760 h/a. The price of Na_2S is estimated from data gained from different commercial sources.

Table 18. Value of the product with different conversion values.

Conversion	**Na_2S produced**	**Price**	**Value**
60 %	3258 ton/a	400 €/ton	1.30 M€/a
80 %	4330 ton/a	400 €/ton	1.73 M€/a
95 %	5142 ton/a	400 €/ton	2.06 M€/a

The estimated value of the product is close to the energy related costs in this process. This would suggest that at the current capacity and sulphate concentration of the retentate the process would not be profitable.

9.1.4 Evaluation and comparison of the results to literature

From the simulation results and the literature examined, it can be deduced that the process concept of carbothermal reduction of sodium sulphate most likely would work in the case studied here. However, in order to be an economically feasible solution the energy economy of the process needs to be very carefully optimised. From the simulated process concept, it is also quite clear that the investment cost, even though it is not covered in this study, can be construed to be rather high. This type of process is also somewhat complex due to many different separation units involved. Therefore, to apply it in commercial scale would take considerable effort and assurance that the production would be maintained for many years.

The energy consumption of the evaporation is somewhat high, when compared to many literature sources. Nafey et al. (2008), for example, state that MEE-MVC system would have approximately the same specific power consumption as an RO system, which is between 6 – 8 kWh/m^3. Therefore, there clearly is room for optimisation. With enhancements in the energy economy, this process can be made more economical. One way of succeed in this would be to utilise the still warm streams from the hot sides of the heat exchangers in the evaporation stages. However, when considering that this process

option also brings with it considerable investment costs, there are risks with this process option.

9.1.4 Uncertainties and error analysis

There are, naturally, uncertainties within this process. These stem mostly from the fact that not enough previous studies related to this type of process exist, especially in this type of application. Biggest uncertainties are related to the actual reduction reaction. The kinetic data on this reaction was found to be scarce and therefore the Gibbs reactor model was used. The yield obtained with the model is quite high (circa 97 % of the Na_2SO_4) and needs to be considered with some caution. The literature found on the subject lists yields between 60 – 95 %. In order to reach the higher end of this gap, the reaction conditions and residence time need to be optimised. Also, the effect of purity of the carbon source used needs to be determined. In this study, this has not been possible.

It is to be noted, that the calculations have been carried out based on the current capacity and composition. These are subject to change, and if a decision is made to run the RO system with higher water recovery rate, this process becomes more feasible because less water needs to be evaporated.

9.2 Results from the laboratory experiments

The results from the laboratory experiments present the sulphate reductions reached with this method. In addition, the effect of $Ca(OH)_2$ and HCl additions on the calcium and sodium concentrations is examined.

9.2.1 Results from the pre-tests

The first pre-test was carried out using just the slaked lime slurry (lime milk) as a reagent and the stirring was manual. Almost immediately after mixing the lime milk with the reject, a powdery white precipitate was visually observed forming and starting to settle in

the reaction vessel. From this occurrence, it can be suspected that the precipitation of gypsum occurs quite rapidly. It is, however hard to make out how much of the precipitate is actually gypsum and how much is undissolved calcium hydroxide. Figure 36 depicts the final concentrations of the key components after the one-hour reaction time. From the severe drop in the sulphate concentration from approximately 11000 mg/l to circa 6500 mg/l it can be deduced that gypsum is precipitated with this method. However, the rise in the alkalinity in the reaction solution creates a limit to the dissolution of the calcium hydroxide caused by the common ion effect. Therefore, the use of $Ca(OH)_2$ alone does not yield required sulphate reductions. The addition of HCl is needed to increase the solubility of $Ca(OH)_2$ and the precipitation of gypsum.

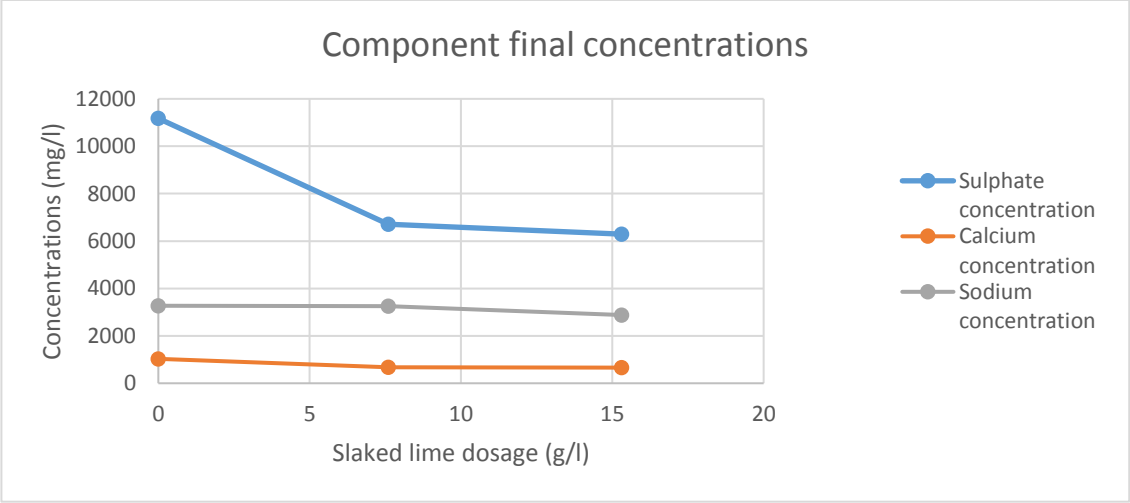

Figure 36. Results from the pre-tests

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9.2.2 Results from precipitation tests

Final sulphate concentrations and reductions

The results from the first set of precipitation tests are in line with the results from the pre-tests, as could be expected. It is clear that the addition of HCl to the reaction mixture increases the solubility of slaked lime and thereafter the amount of gypsum precipitated.

However, the increase in the sulphate reduction does not seem to grow as fast after a certain point. This can be seen in Figure 37.

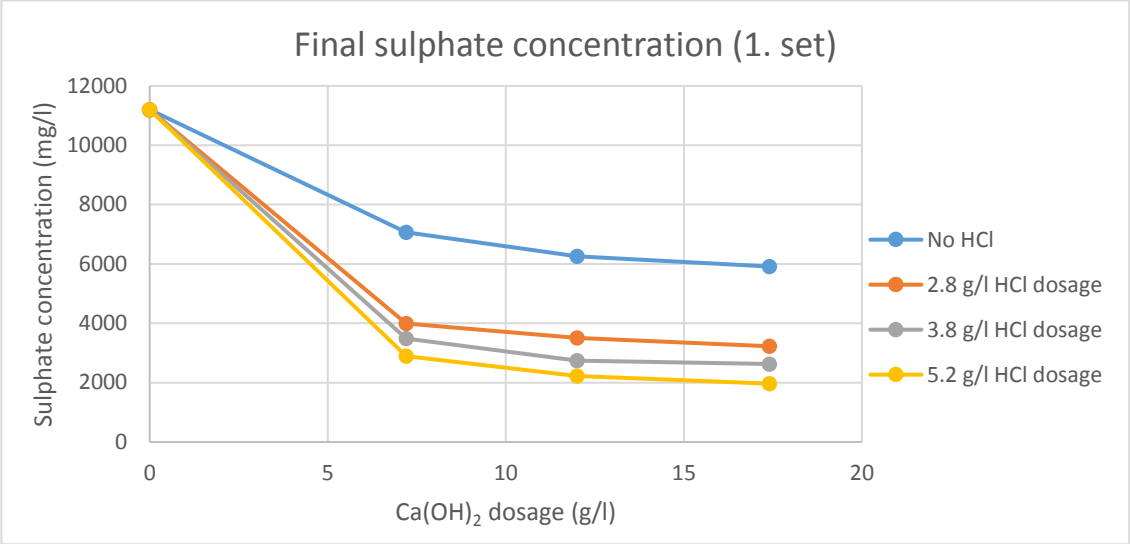

Figure 37. Sulphate concentrations from the precipitation tests carried out on retentate with the original sulphate concentration.

Some of the reduction in the sulphate concentrations comes from the dilution effect from the water contained by the added reagents. Figure 38 shows the actual sulphate reductions in the first set of tests. It can be seen that sulphate reduction is less than 50 percent without the HCl addition but with the addition of HCl, the reduction can be increased so that sulphate reduction close to 80 percent can be reached. It is also clear that the highest dosage of HCl offers relatively small improvement to the reduction percentage. Therefore, a suitable HCl dosage is can be deduced to being close to the second one tried.

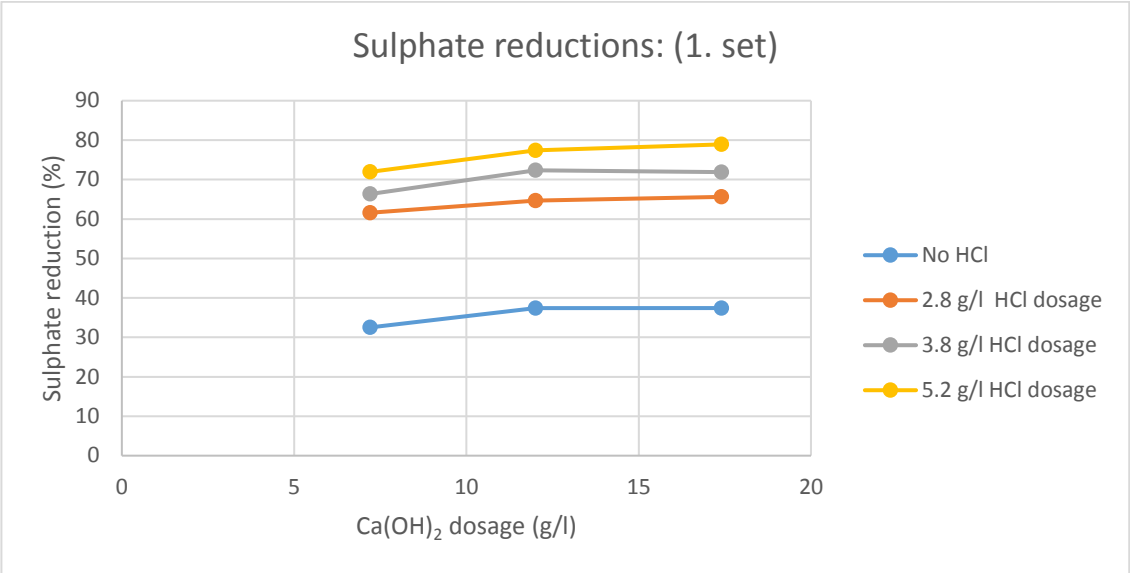

Figure 38. Actual sulphate reductions reached in the first set of tests.

The sulphate results from the second set of precipitation tests, carried out with the concentrated retentate, show similar tendency as the first set of tests (Figure 39). The benefit of the use of HCl is clear but there is a clear point after which increasing the dosage no longer yields significant improvement on the amount of sulphate reduced.

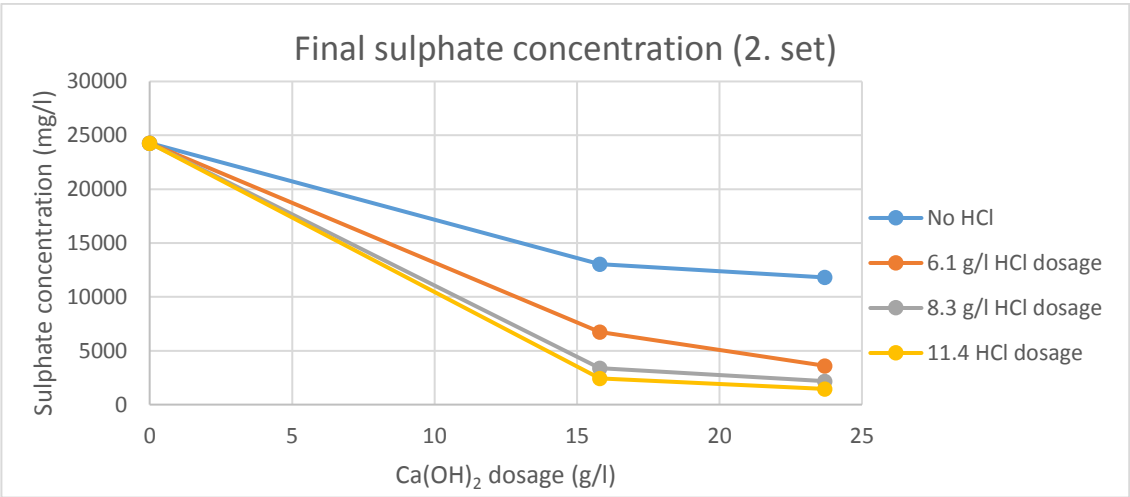

Figure 39. Final sulphate concentration in the second set on precipitation tests.

Figure 40 depicts the sulphate reductions in the second set of experiments. The results are in line with the ones from the first set. The reduction is around 40 % without the addition of HCl and with the neutralising reagent the reduction is close to 90 %. From these results, it is even clearer that the second dosage is the recommendable of the three tried, and that increasing the dosage above it improves the reductions only slightly.

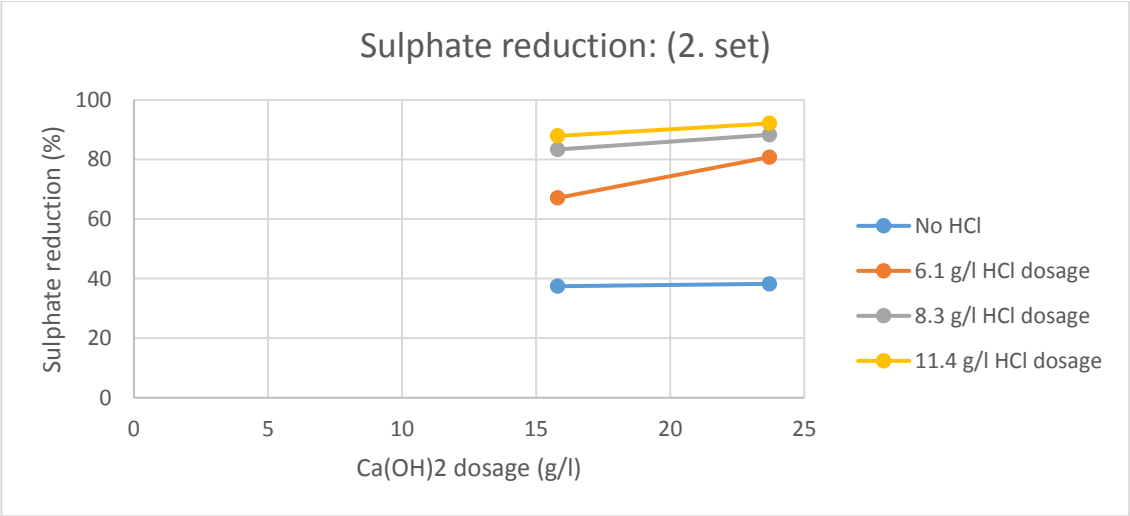

Figure 40. Actual sulphate reductions reached in the second set of tests.

Calcium and sodium final concentrations

From the final calcium concentrations in the treated retentate, it seems clear that the adding of HCl does indeed increase the solubility of $Ca(OH)_2$ (Figure 41). These results show also, that $Ca(OH)_2$ dosage above 1.5 times the stoichiometric amount has little to no effect on sulphate reduction.

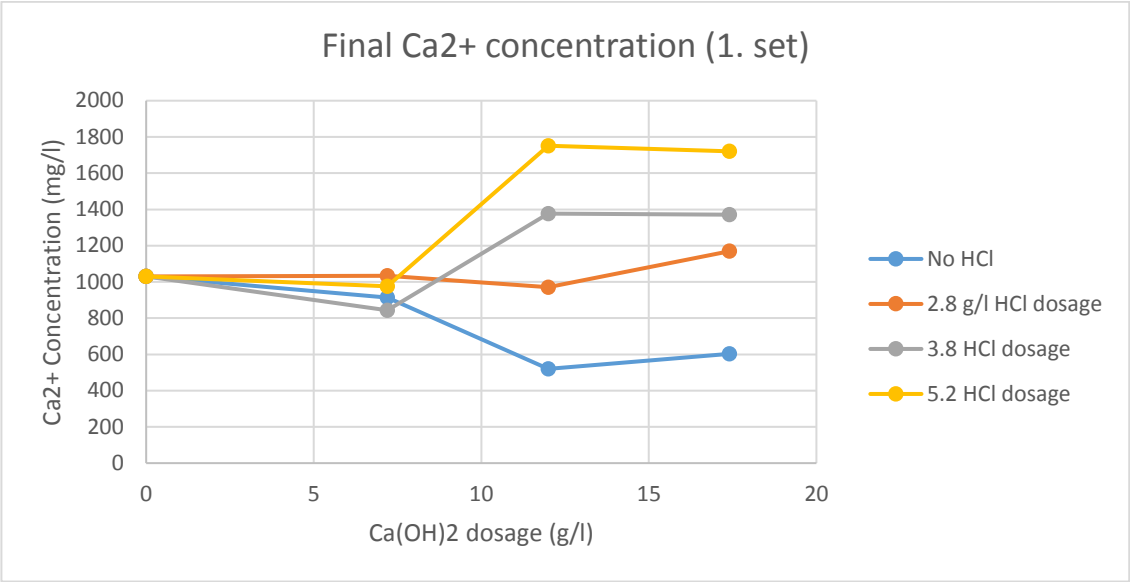

Figure 41. The final calcium concentrations from the precipitation tests carried out on retentate with the original sulphate concentration.

Figure 42 shows that the graphs depicting the final calcium concentrations look slightly different from the graphs in the first set of tests. The lines start dispersing much faster and with a lower $Ca(OH)_2$ dosage than in the first set of tests. The effect of HCl additions in the final concentrations of calcium can be seen in APPENDIX VIII. The second set again seems to be more in line than the first set. Here it should be noted that some of the calcium was precipitated during concentration of the retentate, which can cause some of the discrepancy of the results. The starting solutions in the second set of tests were therefore saturated with gypsum. Therefore, the starting situation differed between sets. Another factor that could contribute to the inconsistencies is the presence of the antiscalant. Because it is concentrated into the retentate along with the salts, it can affect the precipitation. The antiscalant can also have been deactivated during the evaporation between the test sets. This would lead to another difference between the starting solutions in the test sets.

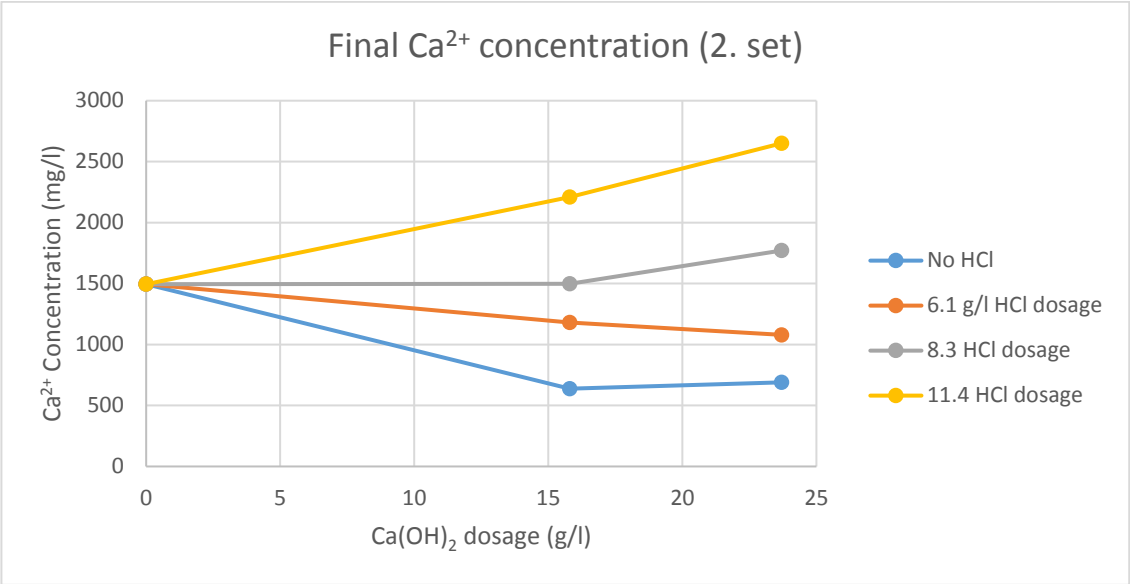

Figure 42. The final calcium concentration in the second set on precipitation tests.

The sodium concentrations seem rather consistent with the two different starting sulphate concentrations tested. They do not vary as greatly as the calcium concentrations, which is to be expected, as sodium is not expected to participate in the precipitation.

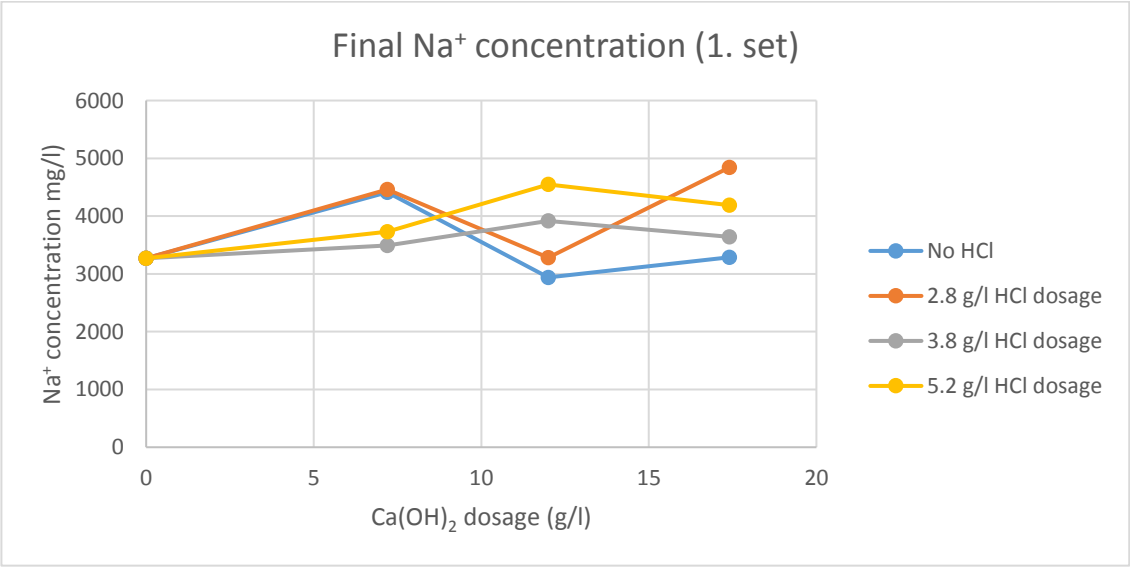

Figure 43. The final sodium concentrations from the precipitation tests carried out on retentate with the original sulphate concentration.

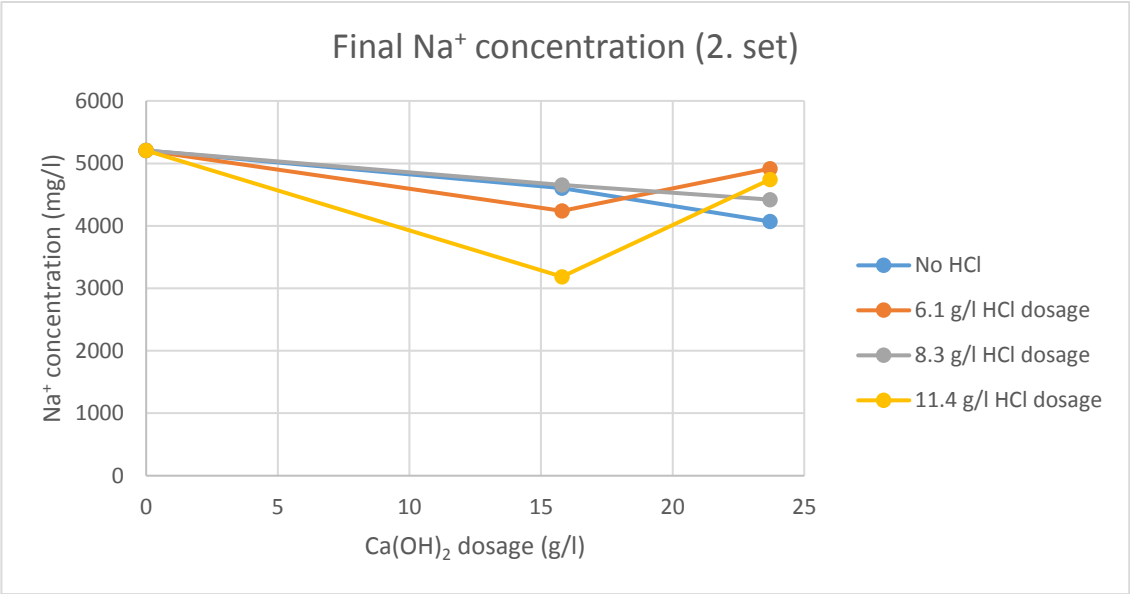

Figure 44. The final sodium concentration in the second set on precipitation tests.

A recommendation for the dosages of the two reagents can be made from the gained results. The recommended dosages are listed in Table 19. They are calculated for the actual sulphate concentration in the retentate. With these dosages, the sulphate reduction reached in the experiments was 72 % and the final sulphate concentration was approximately 2700 mg/l.

Table 19. The recommended dosages for the reagents.

Chemical	**Recommended dosages (g/l)**
$Ca(OH)_2$	12.0
HCl	3.8

9.2.3 Operating costs of the precipitation process

The operating costs are estimated for the current capacity of 100 m^3/h, and sulphate concentration of 11200 mg/l of the retentate stream. The chemical costs from the use of $Ca(OH)_2$ and HCl compose a significant amount of the operating costs. The chemical costs are calculated in Table 20. The precipitating reagent is bought as CaO, which is suspended on-site. The amount of CaO required is calculated from the $Ca(OH)_2$ dosage, which is 12.0 g/l. The price used for CaO is 200 €/ton. The dosage of 32 wt.-% HCl solution is calculated based on the dosage of HCl, which is 3.8 g/l. The price used for the HCl 32 wt.-% solution is 230 €/ton.

Table 20. The Chemical costs for the precipitation

	Amount	**Unit of measure**
Retentate flow	100	m^3/h
SO_4 concentration	11200	mg/l
CaO dosage	9.08	kg/m^3
CaO feed	908	kg/h
CaO price	0.2	€/kg
HCl (32 %) dosage	2.57	kg/m^3
HCl (32%) feed	257	kg/h
HCl (32%) price	0.23	€/kg
Costs	240.71	€/h
	2.1	M€/a

Cooling power is needed due to the exothermic natures of both the dissolution of $Ca(OH)_2$ and the neutralisation of HCl. Some of the heat released is spent on the precipitation of gypsum, which is endothermic. The heats released and consumed are listed in Table 21. They are calculated according to the same capacity and dosages as stated previously. The amounts of reagents participating in the reactions are estimated from the changes in the

amounts of different species in the analysed samples seen in APPENDIX V and APPENDIX VI.

Table 21. Heats of reaction of in the process.

Reaction	**Heat of reaction**	**Heat released/consumed**
Dissolution of $Ca(OH)_2$	−17.23 kJ/mol	−41.9 kJ/s
Neutralisation of HCl	−55.90 kJ/mol	−109.5 kJ/s
Precipitation of $Ca(OH)_2 \cdot 2H_2O$	1.72 kJ/mol	3.6 kJ/s
Total		**−148 kJ/s**

The cooling power required is approximately 150 kW. The energy needed for the cooling is approximately 1314 MWh/a with the cost estimation of 105 120 €. The cost of cooling is quite low when compared to the chemical costs calculated earlier.

9.2.4 Evaluation and comparison of the results to literature

There are well known challenges in using slaked lime in gypsum precipitation. Dissolved calcium ions are consumed from the solution as gypsum is precipitated. Replenishment is required, which is partially taken care of by the dissolution of slaked lime that produces both calcium and hydroxide ions in the solution. The former is removed in the precipitation of gypsum but the latter is not. The concentration of hydroxide ions increases as the sulphate content in the solution decreases. This leads to a pH level so high that the required calcium is no longer dissolved and the K_{sp} of gypsum is no longer exceeded. This phenomenon is seen in practice as a strong decrease in the rate of gypsum precipitation as the pH limit is approached. (Davis et al. 2012) In order to battle this problem, an addition

of hydrochloric acid is used in the experiments. The idea is to neutralise part of the hydroxide ions that build up in the solution.

Another problem with the use of slaked lime is that gypsum has a propensity to precipitate on particles of slaked lime. This leads to the need for excess $Ca(OH)_2$ to make sure that there is enough soluble calcium to surpass the solubility of gypsum. (Davis et al. 2012) A way to try to prevent this could also be to recycle some of the formed gypsum slurry as seed crystals for gypsum precipitation. This would enable the gypsum to precipitate on the seed crystals recycled instead of the slaked lime particles. This could enable a lowering of the required slaked lime dosage.

Also, an important point to remember is the dependency of the solubility of gypsum on pH, which is presented in Figure 31. Solubility increases above pH of circa 11.5 and reaches a maximum at around 12.7, after which the solubility begins to decrease. The rate of gypsum precipitation with $Ca(OH)_2$ can therefore be deduced to being a function of both the pH and the amount of slaked lime present in the system. (Davis et al. 2012) One other problematic factor in the experiments is the presence of the antiscalant used in the RO process. The antiscalant is used to prevent the precipitation of gypsum on the membrane surfaces of the RO system. The substance is concentrated in the retentate stream alongside the salts. Therefore, it is possible that it causes problems during the gypsum precipitation in this study.

Antiscalants have three primary methods for interfering with precipitation. The first is threshold inhibition, in which the antiscalants adsorb to nucleated sub-microscopic crystals. This delays the crystal growth for extended periods or prevents it entirely. Second method is crystals modification, in which the antiscalants' negatively charged groups attack the positive charges found in the crystal nuclei. This leads to interfere with the electronic balance formation of crystals, and the crystals formed are distorted, soft, and non-adherent. The third and last method is dispersion, in which the formed crystals are

surrounded with strong negative charges. The crystals are kept separate from each other by these charges, which prevents aggregation. (Lenntech 2016)

In the study presented by Davies et al. (2012) the reduction of sulphate is close to the reduction reached in this study. The sulphate concentrations reached in this study are actually somewhat lower. Concentrations below 2000 mg/l have been reached, however, it needs to be kept in mind that some of the decrease in the concentration comes from dilution due to reagent additions. To demonstrate this effect, the changes in the actual amount of sulphate in each sample are presented in APPENDIX VII.

9.2.5 Uncertainties and error analysis

One of the uncertainties in the results comes from the reagent used. The $Ca(OH)_2$ slurry is somewhat hard to measure out in exact quantities. This is because the 10 wt.-% slurry used has the tendency to settle quite quickly, which leads to some uncertainty in the exact amount of $Ca(OH)_2$ used. Another important possible source of error in the experiments is the filtration. The system used in the study contains room for improvement. A denser filter would have improved the recovery of the precipitate, for with the used paper some of the precipitate ends up in the filtered solution. An important point is also the chosen method for the chloride analysis, which has its limitations when dealing with low concentrations. The inconsistencies in the final calcium concentrations have not been exhaustively explained with the information in this study. This needs to be kept in mind, when examining the results.

9.3 Comparison of the examined process concepts

Table 22 presents a comparison of the two examined process concepts. The comparison is carried out using a specified set of criteria with different importance factors. The criteria used are operating costs, maturity, environmental aspects, complexity, safety, economic value of the products, sulphate reduction capability. With the maturity of a process is

meant the amount of available information on the process and the ease of applying it in commercial scale. Both of the processes examined are relying on known technology being used in a novel application. However, there is more information to be found as a foundation for designing a process for the process option relying on precipitation. The information about the thermal process is scarce and older. The environmental aspects include the emissions, wastes, as well as the energy requirements. The thermal process concept is, as expected, quite energy intensive and produces both CO and CO_2 emissions. However, it is also a ZLD process, which evens out some of the environmental effects. The precipitation process produces no gaseous emissions and requires less energy, but on the other hand, it produces significant amounts of waste sludge, which requires treatment.

Complexity refers to the total intricacy of the process, which can be measured with, for example, the number of separation units. The thermal option is clearly the more complicated of the two compared. The safety criterion considers both process and operating safety, and also the hazardous properties of both the raw-material and products formed. The economic potential considers the gross margin between raw material and products. Since the precipitation process does not directly produce a product that could be commercialised, it is given a lower score than the thermal process, which produces a product to be used either within the existing operation or sold. The highest importance factor (5) is given to the sulphate reduction capability, because in the end, it is perhaps the most telling factor in this case. The thermal process gains a higher score due to the fact that it is a ZLD, meaning that no soluble sulphates are released into the environment. Based on the test results and literature, the precipitation process also has a significant sulphate reduction capability, which leads to a higher grade in with this criterion.

Table 22. Comparison of different aspects of the process concepts.

Process concept		**Carbothermal reduction**		**Precipitation as gypsum**	
Criterion	**Importance**	**Grade**		**Grade**	
Operating costs	3	6	18	7	21
Maturity	3	6	18	8	24
Environmental aspects	4	8	32	7	28
Complexity	4	6	24	9	36
Safety	3	5	15	8	24
Economic value of the products	3	7	21	5	15
Sulphate reduction capability	5	9	45	7	35
Sum			173		183
Final grade			**6.92**		**7.32**

This comparison gives a general understanding how the process options compare against each other. According to it, the options possess almost the same score and are almost equally well suited. However, attention should also be paid to how these process options fit in with the resources and process already in place. Looking first at the thermal process, it seems clear that this process requires significant investment into new equipment and pipelines. However, the raw material requirements for the process are simple. The main requirement is the carbon source, which in this study has been graphite. Graphite is found in the ore at Terrafame mine and with suitable extraction, it can be utilised. The thermal process produces multiple warm streams that can be utilised. Thermal process is a ZLD process, which means that no liquid waste streams are formed. This would be optimal in the sense that no soluble sulphate comes out of the process. The value of the product formed in the process at the current retentate concentration is low compared to the energy requirements, which indicate that currently, the process is at least not profitable. If, however, the retentate stream were to be more concentrated, the feasibility of the thermal process and the investments it incurs would become better justified. Currently, in

conjunction with the previously stated, the risks related to the lack of exact data suggest that the thermal process not be studied further.

The process based on gypsum precipitation can be understood as the safer and surer option of the two, also when looking at the existing process. First of all, the precipitation does not require any pre-treatment or concentration of the retentate. Therefore, it is simpler to implement. Also, the fact that similar type of precipitation method is already used at the mine site, makes this process option easier to integrate into the existing operation. The treatment of the precipitate formed can also be done in a similar way as in the existing process. Biggest questions to be answered relate to the use of HCl as a reagent and the presence of antiscalant in the retentate. There exists no limit to the amount of chloride in mine water, which would seem to favour the use of HCl. Also, the results from laboratory tests, especially the sulphate reductions, would suggest that the negative effect of antiscalant on gypsum precipitation is minor and does not pose a serious obstacle to this process option. However, the effect of time on the effectivity of antiscalant should be studied, because in the tests in this study were carried out several weeks after the retentate sample was collected.

10 Conclusions and recommendations

10.1 Conclusions

As was discovered in the literature study, the reduction of sulphate from the retentate stream is technologically possible. There exists a number of different treatment options, which could be applied in this case. The scope of this study was to estimate the feasibility of two of these processes. The process utilising carbothermal reduction, according to literature and the simulation results, appears to be a very effective way of reducing sulphate concentration. However, as was discovered, it is a very energy intensive process, mainly due to the leanness of the retentate. In addition, the lack of starting information for modelling the reaction leads to a need for laboratory and pilot scale testing to determine the suitability of the method for this application. Especially the kinetic data found about the reaction was scarce and often tied to a specific case and not applicable as such in this case. All in all, the results from the simulations and the estimations about the operating expenses suggest that this method is not economically feasible with the current retentate concentrations.

Of the two process concepts examined in this study, the one relying on precipitation was found to be a safer and also simpler option, as there exists more literature and actual test results available on it. In favour of the precipitation process is also the fact that lime precipitation is already in use at the mine site. Therefore, some of the equipment needed for it are already in place and the process components are quite well known already.

The results gained in this study show that the reduction of the sulphate level in the retentate can be achieved with many different methods and combinations of them. Two possible methods were shown to be effective in the reduction of sulphate. Both options, carbothermal reduction and gypsum precipitation, can be considered viable for the mining operation examined in this study. Both can be integrated to the existing operation and in

conjunction with improvements in the existing RO system would lead to significant reductions in the sulphate load.

The second goal related to recycling was not reached as successfully as the first goal related to sulphate reduction. The carbothermal process offers a way to gain Na_2S as product, which could be used as one of the sulphide precipitation reagents in the metal recovery process. Alternatively, the product could be sold. The process based on gypsum precipitation offered less impressive recycling possibilities. The water with reduced sulphate content can be recycled within the process, but the idea of concentrating NaOH in the retentate was unsuccessful due to the low sulphate reduction reached using only the slaked lime.

10.2 Limitations and recommendations

The results gained in the applied part of this study are based on the specific process and its conditions in the Sotkamo mine. Conclusions that are more general need to be drawn with caution. It is also important to remember that the period during which the retentate is examined is relatively short (2 – 3 months), and that due to the nature of the mining process the quality and composition of the retentate may vary. The starting information about the process is also tied to the period during which this study was conducted. Possible changes made to the process and especially in the RO system need to be assessed when looking at the results.

The results from the simulated process should be considered mainly guiding. This is due to the lack of experimental data of the very process. In order to gain more accurate information, especially about the reaction kinetics, pilot testing is necessary. Also, more information about the scaling problems during the evaporation and concentration of the retentate are needed. This study presents a starting point from which this process concept can be developed further. The exact effect of antiscalant to the precipitation of gypsum should be examined more closely to determine if the sulphate reduction can be enhanced

by either deactivating the antiscalant or by removing it from the retentate and possibly regenerating it. Lastly, there are some recommendations based on observations made during this project, which would be useful when moving forward with the water treatment in the mining site. These recommendations are listed below.

- A comprehensive water and chemical balances of the process were missing during this project; they are paramount in future development plans for water treatment.
- An overall optimisation of the RO plant would help to stabilise the quality of the retentate, which makes the
- The ratio with which the RO plant is run should be studied further and the amount of pure water grown if possible. This is because both processes examined in this study suggest that using more concentrated retentate yields better results.
- The effect and amount of antiscalant used in the RO system should be studied and optimised. If the amount used in the operation can be lower, it would significantly lower the costs of the RO plant, while at the same time could enhance the sulphate reduction in the precipitation process.
- Carbothermal reduction can become a more viable option if the RO is run with a higher permeate portion and the retentate is more concentrated. The amount of Na_2S produced, and therefore the possible revenue generated, is dependent on the amount of Na_2SO_4 in the retentate.
- The precipitation appears a ready and suitable method for lowering the sulphate load in the retentate. It seems very recommendable to investigate this method more profoundly in the near future.

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APPENDIX I Comparison of the retentate treatment options

Technology	Feed requirements	Sulphate removal efficiency	Technological maturity
Membrane methods			
FO	not available	not available	pilot scale
ED	pre-treatment required (fouling), no calcium in the feed	not available	pilot plant scale/full scale
BMED	pre-treatment required (fouling & microbial growth prevention)	not available	pilot plant scale
Biological methods			
Bioreactor	pre-treatment required	Below 300 mg/l	used in smaller scale
Membrane bioreactors	pre-treatment required	not available	used in smaller scale
Precipitation methods			
Ion exchange (GYP-CIX)	any pH level	sulphate content reduced below 50 mg/l	pilot plant testing done
(Integrated) Lime and limestone precipitation	acidic or neutral conditions	sulphate content reached 1500 - 2000 mg/l, with integrated process sulphate content of 1200 mg/l has been reached	mature technology
Barium salt precipitation	for $BaCO_3$ mildly acidic, for BaS and BaOH every pH level	With BaS, sulphate content of 190 mg/l reached	Mature technology
Ettringite precipitation	pH level of 10 - 12	sulphate content below 200 mg/l reached	mature technology
Jarosite precipitation	acidic conditions, needs an iron source	not determined	not in use
Thermal processes			
Evaporation Crystallisation	no special feed requirements	varies	full scale
Carbothermic reduction	sulphate being reduced in solid state	not available	mature technology
Eutectic freeze crystallisation	no pressure requirements	complete phase change	pilot plant scale, not proven to work on commercial scale

APPENDIX I Comparison of the retentate treatment options

Technology	Costs	Chemical recycling	Advantages
Membrane methods		varies	less enegy intensive than thermal processes
FO	not available	recycling of the draw solution	low or no hydraulic operating pressures, rejects a large range of contaminants, lower membrane-fouling tendency than pressure-driven membrane-processes, simple equipment
ED	for EDR: Capital cost $ 23, 070/m^3/h, Chemical costs $0.07/m^3	possible	production of sellable by products
BMED	for EDR: Capital cost $ 23, 070/m^3/h, Chemical costs $0.07/m^3	possibility of both acid and base recycling	able to recycle both NaOH and H2SO4
Biological methods			
Bioreactor	Capital cost $ 0.24 M per 10 m^3/day, Operating costs $ 0.27 /m^3 (delta SO4 = 2000 mg/l)	H2S, elemental S, and CO2 recycling	low volume of sludge, recovery of base metals as sulfides
Membrane bioreactors	not available	not available	low volume of sludge, recovery of base metals as sulfides, no sedimentation tank needed, avoidance of biological treatment stages
Precipitation methods			
Ion exchange (GYP-CIX)	depend on the quality of feed and product water, 86 % of total oper. Costs come from costs of regenerants	regeneration of the resins used	regeneration of resins using low cost chemicals, lowering of TDS and corrosion
(Integrated) Lime and limestone precipitation	capital cost unknown (low), Operating cost $ 0.10/m^3	in the integrated process, limestone can be recycled back to the process	BAT, low to moderate amount of monitoring
Barium salt precipitation	BaS: capital cost $ 0.48 M per 10^3/day, Operating costs $ 0.36 /m^3 (delta SO4 = 2000 mg/l)	BaS can be regenerated using thermal reduction	high sulphate rejection
Ettringite precipitation	SAVMIN: Capital cost $ 0.31 M per 10 m^3 /day, Operating costs $ 0.17 m^3	Al(OH)3 can be recycled by regeneration from ettringite slurry (SAVMIN)	high quality of product water
Jarosite precipitation	not available	jarosite recycled as seed crystals	binds both sodium and sulphate
Thermal processes			
Evaporation Crystallisation	$ 33, 000/m^3/h(Capital) $ 0.01/m^3 (Chemicals)	depends on the purity of the salts recovered	reliable and known technology
Carbothermic reduction	not available	recycling of Na_2S	ZLD process, recycling of Na Na_2S
Eutectic freeze crystallisation	Capital cost 179 - 208 % higher than for evaporative crystallisation, operating costs expencted to be substancially lower	salts can be recycled	pure salts as products, low energy requirements, no feed pressure requirements, no added chemicals

APPENDIX I Comparison of the retentate treatment options

Technology	Disadvantages
Membrane methods	restrictions with water of more complex quality
FO	requires a draw solution, limited full-scale applications, increased energy consumption with draw solution recovery
ED	maintaining energy efficiency with high saline concentrates, precepitation on membrane, high capital and operation cost
BMED	limited stability of ion-exchange membranes with strong acids and bases, possibility of product contamination, costly membranes
Biological methods	
Bioreactor	cost of C + energy source, production of various sludges, Possible toxicity effects of wastestream on SRB, inhibition caused by high cation (NA+ and Ca2+) concentrations
Membrane bioreactors	sensitive to temperature, high initial investment cost, energy demand for pumping water through membranes
Precipitation methods	
Ion exchange (GYP-CIX)	economically best suited for waters with sulphate content below 1500-2000, gypsum sludge produced in the regeneration of ion-exchange resins
(Integrated) Lime and limestone precipitation	limited sulphate removal, production of sludges
Barium salt precipitation	barium salts are quite expensive, toxicity
Ettringite precipitation	production of sludges
Jarosite precipitation	limited applications for the produced jarosite product, limited information on the stability of the product compound
Thermal processes	
Evaporation Crystallisation	large investment and possible operating costs, often not feasible
Carbothermic reduction	high temperatures, energy intensive process
Eutectic freeze crystallisation	not yet proved to work in commercial scale

APPENDIX II Stream table of the first scenario simulated with Aspen

Stream ID		F	C1	S1	V1	B1	CASO4	NA2SO4	S2	C2	S3	V2	B2	S4	C3	S5	V3	B3
Mass Flow	KG/H	100743	24547.6	100743	23095.22	77647.78	304.64	77343.14	77343.14	23095.22	77343.14	23820.82	53522.32	53522.32	23820.82	53522.32	24351.67	29170.65
Mass Enthalpy	MW	-441.91	-106.20	-426.02	-85.14	-332.21	-0.89	-331.33	-331.33	-99.47	-317.00	-87.89	-229.11	-229.11	-102.77	-214.23	-89.93	-124.29
Mass flow rate																		
H2O	KG/H	99253.19	24547.6	99303	23095.22	76207.78	0	76207.78	76207.78	23095.22	76207.78	23820.82	52386.96	52386.96	23820.82	52386.96	24351.67	28035.29
CO	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO2	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CA++	KG/H	38.80	0	5.17	0	4.52	0	4.52	4.52	0	4.15	0	4.15	4.52	0	3.39	0	3.39
NA+	KG/H	362.54	0	362.54	0	362.54	0	362.54	362.54	0	362.54	0	362.54	362.54	0	362.54	0	362.54
CASO4(S)	KG/H	0	0	302.43	0	304.64	304.64	0.00031	0	0	1.24	0	1.24	0	0	3.85	0	3.85
CASO4·2H2O(s)	KG/H	238.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na2SO4(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na2SO4·2H2O(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA2S(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO4--	KG/H	850.46	0	769.87	0	768.30	0	768.30	768.30	0	767.42	0	767.42	768.30	0	765.58	0	765.58
S--	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2SO4	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2S	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA2CO3	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CACO3(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO2	KG/H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Volume flow rate. mixture	M3/H	99.67	25.56	10196.83	25490.37	80.60	0.10	80.50	1265.68	24.36	31949.79	31894.69	55.11	1302.83	25.00	41663.58	41634.18	29.40
Mass vapor fraction		0	0	0.091	1	0	0	0	0.011	0	0.31	1	0	0.014	0	0.45	1	0
Mass solid fraction		0.0024	0	0.0030	0	0.0039	1	3.99E-09	0	0	1.61E-05	0	2.33E-05	0	0	7.20E-05	0	0.00013
Density. mixture	KG/M3	1010.73	960.27	9.88	0.91	963.34	2963.47	960.79	61.12	948.12	2.42	0.75	971.23	41.08	952.87	1.28	0.58	992.26
Temperature	C	25	97.01	113.41	113.47	113.47	113.47	113.47	107.27	113.34	107.32	107.32	107.32	99.80	107.14	99.93	99.93	99.93
Pressure	BAR	1.6	0.91	1.60	1.6	1.6	1.6	1.6	1.3	1.6	1.3	1.3	1.3	1	1.3	1	1	1

APPENDIX II Stream table of the first scenario simulated with Aspen

Stream ID		S6	C4	S7	V4	HOT	B4	V5	SALT	C	P
Mass Flow	KG/H	29170.65	24351.7	29170.65	24547.58	24547.58	4623.06	2400.02	2223.04	740	2963.04
Mass Enthalpy	MW	-124.29	-105.28	-108.95	-90.75	-90.31	-18.20	-8.90	-7.82	-5.57E-17	-3.59
Mass flow rate											
H2O	KG/H	28035.29	24351.7	28035.29	24547.58	24547.58	3487.70	2400.02	1087.69	0	1085.65
CO	KG/H	0	0	0	0	0	0	0	0	0	870.25
C	KG/H	0	0	0	0	0	0	0	0	740	361.30
CO2	KG/H	0	0	0	0	0	0	0	0	0	15.33
CA++	KG/H	4.40	0	1.14	0	0	1.14	0	0.55	0	0
NA+	KG/H	362.54	0	362.28	0	0	362.28	0	126.32	0	0
CASO4(S)	KG/H	0.40	0	11.48	0	0	11.48	0	13.48	0	7.52E-16
CASO4·2H2O(s)	KG/H	0	0	0	0	0	0	0	0	0	0
Na2SO4(S)	KG/H	0	0	0.79	0	0	0.79	0	729.74	0	3.44E-27
Na2SO4·10H2O(S)	KG/H	0	0	0	0	0	0	0	0	0	0
NA2S(S)	KG/H	0	0	0	0	0	0	0	0	0	615.38
SO4--	KG/H	768.02	0	759.66	0	0	759.66	0	265.26	0	0
S--	KG/H	0	0	0	0	0	0	0	0	0	0
H2SO4	KG/H	0	0	0	0	0	0	0	0	0	3.10E-23
H2S	KG/H	0	0	0	0	0	0	0	0	0	3.84
NA2CO3	KG/H	0	0	0	0	0	0	0	0	0	3.32E-12
CACO3(S)	KG/H	0	0	0	0	0	0	0	0	0	11.29
SO2	KG/H	0	0	0	0	0	0	0	0	0	7.05E-10
Volume flow rate. mixture	M3/H	1214.28	25.41	58804.97	58801.13	49477.64	3.86	12680.82	1.48	0.33	12654.7
Mass vapor fraction		0.017	0	0.84	1	1	0	1	0	0	0.84
Mass solid fraction		1.36E-05	0	0.00042	0	0	0.0027	0	0.33	1	0
Density. mixture	KG/M3	24.02	958.40	0.50	0.42	0.50	1197.69	0.19	1506.22	2267.08	0.23
Temperature	C	90.24	99.63	92.07	92.07	126.41	92.07	71.20	71.20	25	950
Pressure	BAR	0.7	1	0.7	0.7	0.91	0.7	0.3	0.3	1	1

APPENDIX III Stream table of the second scenario simulated with Aspen

Stream ID		F	C1	S1	V1	B1	S2	C2	S3	V2	B2	S4
Mass Flow	KG/H	50771.5	15498.15	50771.5	15103.42	35668.08	35668.08	15103.42	35668.08	15394.58	20273.51	20273.51
Mass Enthalpy	MW	-222.00	-66.86	-212.07	-55.68	-151.85	-151.85	-65.05	-142.48	-56.80	-85.68	-85.68
Mass flow rate												
H2O	KG/H	49651.5	15498.15	49651.5	15103.42	34548.08	34548.08	15103.42	34548.08	15394.58	19153.5	19153.5
CO	KG/H	0	0	0	0	0	0	0	0	0	0	0
C	KG/H	0	0	0	0	0	0	0	0	0	0	0
CO2	KG/H	0	0	0	0	0	0	0	0	0	0	0
CA++	KG/H	0	0	0	0	0	0	0	0	0	0	0
NA+	KG/H	362.54	0	362.54	0	362.54	362.54	0	362.54	0	362.54	362.54
CASO4(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0
NA2SO4(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0
NA2SO4·10H2O(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0
NA2S(S)	KG/H	0	0	0	0	0	0	0	0	0	0	0
SO4--	KG/H	757.46	0	757.46	0	757.46	757.46	0	757.46	0	757.46	757.46
S--	KG/H	0	0	0	0	0	0	0	0	0	0	0
H2SO4	KG/H	0	0	0	0	0	0	0	0	0	0	0
H2S	KG/H	0	0	0	0	0	0	0	0	0	0	0
NA2CO3	KG/H	0	0	0	0	0	0	0	0	0	0	0
Volume flow rate. mixture	M3/H	49.91	16.26	8663.66	16675.94	36.58	573.46	15.93	20647.99	20627.73	20.26	476.41
Mass vapor fraction		0	0	0.1533953	1	0	0.0112518	0	0.4316065	1	0	0.0131666
Mass solid fraction		0	0	0	0	0	0	0	0	0	0	0
Density. mixture	KG/M3	1017.28	952.87	5.86	0.91	975.07	62.20	948.12	1.73	0.75	1000.66	42.55
Temperature	C	25	107.14	113.48	113.61	113.61	107.41	113.34	107.60	107.60	107.60	100.10
Pressure	BAR	1.6	1.3	1.6	1.6	1.6	1.3	1.6	1.3	1.3	1.3	1

APPENDIX III Stream table of the second scenario simulated with Aspen

Stream ID		**C3**	**S5**	**V3**	**HOT**	**B3**	**V5**	**SALT**	**C**	**P**
Mass Flow	KG/H	15394.58	20273.51	15498.15	15498.15	4775.35	2400.14	2375.21	740	3115.21
Mass Enthalpy	MW	-66.42	-76.06	-57.22	-56.93	-18.84	-8.90	-8.50	-5.57E-17	-4.13
Mass flow rate										
H2O	KG/H	15394.58	19153.5	15498.15	15498.15	3655.35	2400.14	1255.21	0	1255.21
CO	KG/H	0	0	0	0	0	0	0	0	864.72
C	KG/H	0	0	0	0	0	0	0	740	365.19
CO2	KG/H	0	0	0	0	0	0	0	0	14.71
CA++	KG/H	0	0	0	0	0	0	0	0	0
NA+	KG/H	0	362.54	0	0	362.54	0	145.76	0	0
CASO4(S)	KG/H	0	0	0	0	0	0	0	0	0
NA2SO4(S)	KG/H	0	0	0	0	0	0	669.70	0	3.46E-27
NA2SO4·10H2O(S)	KG/H	0	0	0	0	0	0	0	0	0
NA2S(S)	KG/H	0	0	0	0	0	0	0	0	615.3841
SO4--	KG/H	0	757.46	0	0	757.46	0	304.54	0	0
S--	KG/H	0	0	0	0	0	0	0	0	0
H2SO4	KG/H	0	0	0	0	0	0	0	0	0
H2S	KG/H	0	0	0	0	0	0	0	0	2.05E-06
NA2CO3	KG/H	0	0	0	0	0	0	0	0	6.39E-06
Volume flow rate. mixture	M3/H	16.16	26633.36	26629.31	22401.16	4.06	12681.27	1.63	0.33	13629.16
Mass vapor fraction		0	0.76	1	1	0	1	0	0	0.85
Mass solid fraction		0	0	0	0	0	0	0.28	1	0
Density. mixture	KG/M3	952.87	0.76	0.58	0.69	1177.47	0.19	1454.38	2267.08	0.23
Temperature	C	107.14	101.76	101.76	136.92	101.76	71.19	71.19	25	950
Pressure	BAR	1.3	1	1	1.3	1	0.3	0.3	1	1

Sodium: Atomic absorption spectroscopy (AAS)

The sodium concentration of the samples is measured with Varian AA240 – machine using air – acetylene flame atomisation. CsCl solution is added to the samples in order to prevent the ionisation of sodium. The measuring wavelength used is 589 nm. The standards are prepared from 1000 ppm storage solution (ACCU standards).

Calcium and sulphur: ICP

The sulphur and calcium concentrations of the samples are determined using Perkin Elmer DV-7100 ICP OES –machine. The measuring wavelength for calcium is 317.933 nm and the control wavelength is 315.887 nm. For sulphur, the measuring wavelength is 181.975 nm and the control wavelength is 180.669 nm. The standards are prepared from 1000 ppm storage solution (ACCU standards).

Chloride: Gravimetric method

The chloride ions in the solutions are analysed using a gravimetric method. This entails adding silver nitrate to the sample that has been acidified with nitric acid in order to precipitate the chloride ions as silver chloride. The formed precipitate is thereafter filtered to a dried and weighed filter paper. The precipitate is dried overnight in an incubator after which the precipitate is weighed and the original chloride concentration is determined from the amount of silver chloride produced. This analysis method can be somewhat inaccurate when dealing with relatively small concentrations, as is the case here. This needs to be taken into consideration when analysing the results.

Analysis of the formed precipitate

The precipitate formed in the laboratory experiments is analysed in order to make sure that the sulphate, calcium, and sodium balances match. The formed precipitate is dried and weighed into Teflon containers, into which HCl is added. The containers are closed and heated in the microwave oven for an hour in 200 °C. After this, the sample is cooled and diluted. Sodium ions are measured using AAS, and sulphur and calcium using ICP.

APPENDIX V Results from the first set of precipitation tests

Samples: IDs and dosages of each sample					Results: The concentrations and actual amounts of components in the solutions							
ID	**Ca(OH)2 dosage g/l**	**Ca(OH)2 dosage ml**	**HCl dosage g/l**	**HCl dosage ml**	**SO4 (mg/l)**	**SO4 (mg)**	**Ca (mg/l)**	**Ca (mg)**	**Na (mg/l)**	**Na (mg)**	**Cl (mg/l)**	**Cl (mg)**
0*	0	0	0	0	11200	2240	1030	206	3270	654	-	-
1	7.2	14	0	0	7063.681	1511.6	912.8	195.3	4412.52	944.3	1050	224.7
2	12	24	0	0	6260.418	1402.3	520.1	116.5	2939.16	658.4	2200	492.8
3	17.4	37	0	0	5914.365	1401.7	603.4	143	3284.4	778.4	2050	485.9
4	7.2	14	2.8	1.6	3991.148	860.5	1033.9	222.9	4459.56	961.5	4100	884
5	7.2	14	3.8	2.2	3487.798	754.1	843.5	182.4	3492.72	755.1	5200	1124.2
6	7.2	14	5.2	3	2896.361	628.5	975.8	211.7	3727.08	808.8	5600	1215.2
7	12	24	2.8	1.7	3508.77	791.9	970.9	219.1	3280.2	740.3	4350	981.8
8	12	24	3.8	2.3	2736.967	619.4	1376.9	311.6	3916.08	886.2	5550	1256
9	12	24	5.2	3	2225.227	505.1	1751.4	397.6	4547.76	1032.3	5050	1146.4
10	17.4	37	2.8	1.8	3225.636	770.3	1169	279.2	4840.92	1156	3900	931.3
11	17.4	37	3.8	2.4	2627.908	629.1	1370.6	328.1	3643.08	872.2	4800	1149.1
12	17.4	37	5.2	3.3	1965.163	472.2	1719.9	413.3	4191.6	1007.2	4950	1189.5

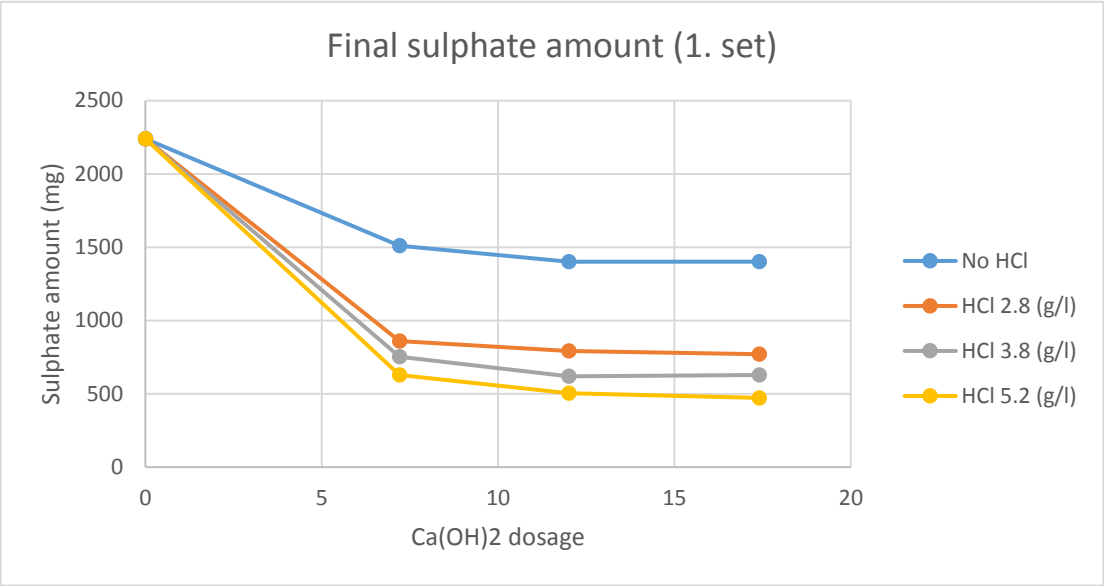
*The zero sample

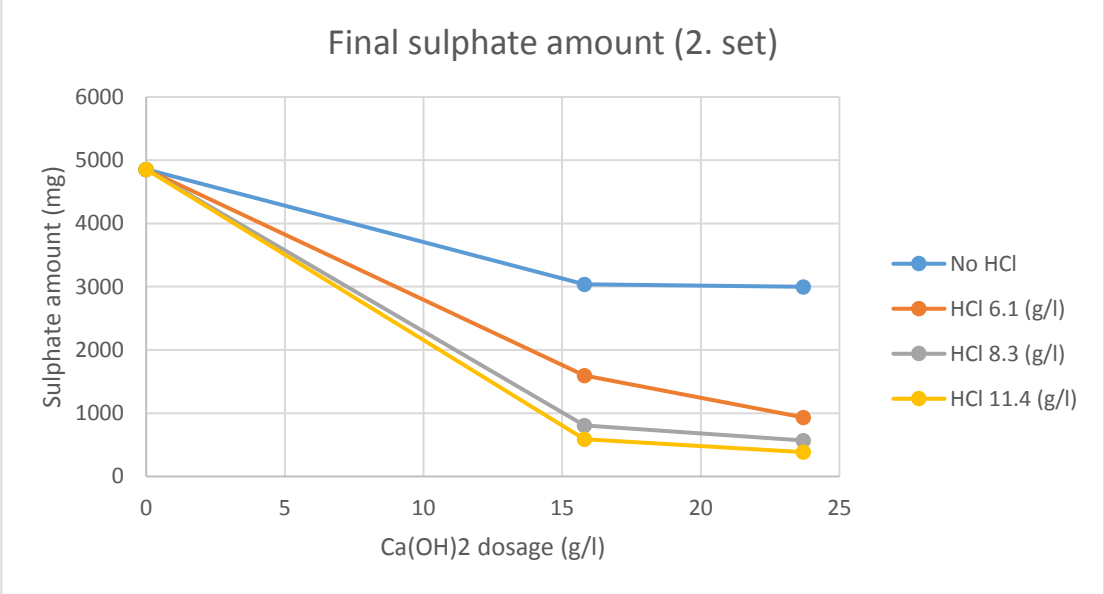
APPENDIX VI Results from the second set of precipitation tests

Samples: IDs and dosages of each sample					Results: The concentrations and actual amounts of components in the solutions							
ID	**Ca(OH)2 dosage g/l**	**Ca(OH)2 dosage ml**	**HCl dosage g/l**	**HCl dosage ml**	**SO4 (mg/l)**	**SO4 (mg)**	**Ca (mg/l)**	**Ca (mg)**	**Na (mg/l)**	**Na (mg)**	**Cl (mg/l)**	**Cl (mg)**
1*	0	0	0	0	24283.6519	4856.730381	1495	299	5205.6	1041.12	600	120
2	15.8	33	0	0	13040.66563	3038.475091	638	148.654	4605.6	1073.105	770	179.41
3	23.7	54	0	0	11807.75721	2999.17033	689.5	175.133	4069.2	1033.577	570	144.78
4	15.8	33.4	6.1	3.9	6735.305303	1598.287948	1180	280.014	4239.6	1006.057	6400	1518.72
5	15.8	33.7	8.3	5.3	3385.629445	809.1654373	1499	358.261	4652.4	1111.924	8170	1952.63
6	15.8	34	11.4	7.3	2435.855521	587.7719372	2210	533.273	3186	768.7818	8050	1942.465
7	23.7	54.8	6.1	4.2	3604.347099	933.5258987	1079.5	279.5905	4916.4	1273.348	6100	1579.9
8	23.7	55.2	8.3	5.8	2179.686213	568.8981017	1771	462.231	4419.6	1153.516	7950	2074.95
9	23.7	55.8	11.4	8	1457.618341	384.5197183	2650.5	699.2019	4741.2	1250.729	8220	2168.436

*The zero sample

APPENDIX VII Final sulphate amounts





APPENDIX VIII Final calcium amounts (as functions of HCl dosage)